SOME INTERESTING STUDIES OF MONO — AND DIORGANOBORANES

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

by

V. V. RAMANA RAO

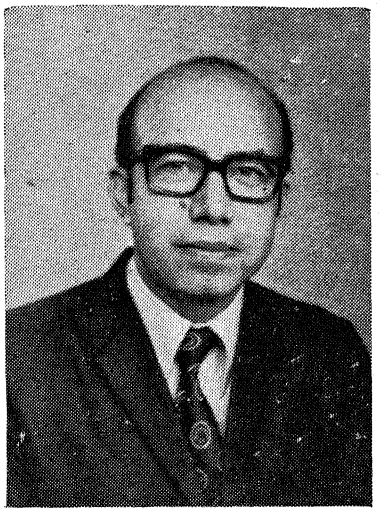
to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

APRIL, 1979

Dedicated to



(Late) Professor D. Devaprabhakara

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India under the supervision of (late) Professor D. Devaprabhakara and Dr. S. Chandrasekaran.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE I

This is to certify that Mr. V.V. Ramana Rao has satisfactorily completed all the courses required for the Ph.D. degree programme in Chemistry. These courses include:

Chm 500 Basic Course in Mathematics

Chm 501 Advanced Organic Chemistry I

Chm 502 Advanced Organic Chemistry II

Chm 521 Chemical Binding

Chm 523 Chemical Thermodynamics

Chm 524 Modern Physical Methods in Chemistry

Chm 541 Advanced Inorganic Chemistry I

Chm 618 Frontier Topics in Organic Chemistry.

Chm 800 General Seminar

Chm 801 Graduate Seminar

Chm 900 Graduate Research

Mr. V.V. Ramana Rao has successfully completed his qualifying examination in January 1977.

(S. Ranganathan)
Head,
Department of Chemistry

(S. Mukherji)
Convener,
Departmental Post-Graduate

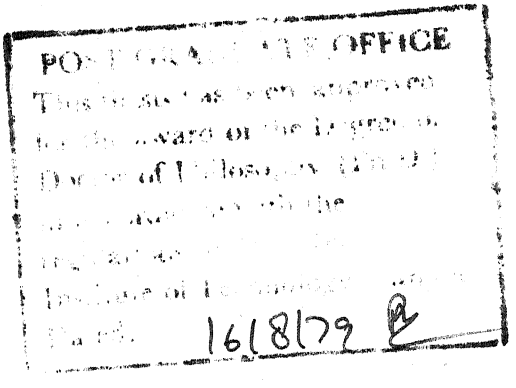
CERTIFICATE II

Certified that the work contained in this thesis entitled "Some Interesting Studies of Mono- and Diorgano-boranes" has been carried out by Mr. V.V. Ramana Rao, under the supervision of (late) Professor D. Devaprabhakara. After his expiry in January 1978 he continued to work in the same field under my supervision and the same has not been submitted elsewhere for a degree.

S. Chandrasekaran

S. Chandrasekaran
Thesis Supervisor

Kanpur,
April 1979.



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V.V. Ramana Rao

CONTENTS

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PREFACE

The thesis entitled, 'SOME INTERESTING STUDIES OF MONO- AND DIORGANOBORANES' consists of five chapters. Each of the five chapters, is further subdivided into five parts, namely, (1) Abstract, (2) Introduction, (3) Results and Discussion, (4) Experimental, and (5) References.

The introduction part of the I Chapter outlines a brief survey of the hydroboration reaction in general and electrophilic additions and conformational behaviour of caryophyllene and isocaryophyllene. The monohydroboration of caryophyllene with dicyclohexylborane followed by oxidation brought about the participation of the (E)-trisubstituted double bond in preference to the exocyclic double bond during hydroboration to the corresponding unsaturated alcohol. This alcohol gave the corresponding ketone by oxidation with pyridinium chlorochromate. Isocaryophyllene under similar conditions provided the unsaturated alcohol as the major product, wherein the participation of the exocyclic double bond took place during hydroboration. Our attempts to achieve cyclic hydroboration with caryophyllene or isocaryophyllene using thexylborane resulted in the formation of the corresponding unsaturated alcohol. We achieved partial regioselective reduction of caryophyllene and isocaryophyllene with diimide to produce the corresponding dihydroderivative.

The introductory part of Chapter II deals with the chemistry of 1,1- and 1,2-diorganoboranes. Representative acetylenes like, diphenylacetylene, 5-decyne, cyclotridecyne and 1-phenylpropyne were dihydroborated using BH_3-THF, and the resulting mixture of 1,1- and 1,2-diorganoboranes was treated with chromium trioxide in pyridine. It appears that the 1,1-diorganoboranes are transformed to the corresponding alcohols and ketones, while the 1,2-diorganoboranes mainly give (E)-olefins *via* a *cis*-stereospecific elimination. Thus the amount of (E)-olefins isolated directly indicates, 1,2-diorganoborane while ketone and alcohol put together give the amount of 1,1-diorganoborane. The relative amounts of 1,1- and 1,2-diborocompound obtained from different acetylenes is well in agreement with steric and electronic requirement of the parent acetylenes and intermediate monoorganoboranes.

The chromic acid oxidation of organoboranes from olefins and dienes forms the introduction to Chapter III. Organoboranes from medium ring olefins and (E)-4-octene on oxidation with an excess of pyridinium chlorochromate in dichloromethane provides ketones in good yield. We believe that the oxidation of organoboranes with pyridinium chlorochromate proceeds *via* the formation of alcohols which subsequently get oxidized to ketones. The anhydrous reaction conditions and easy work-up procedure employed in this reaction, thus make it a convenient one step procedure for the oxidation of alkenes to ketones in high yield.

The mono- and dihydroboration of cyclic and acyclic allenes with diborane and monohydroboration of cyclic and acyclic allenes with disiamylborane, 9-borabicyclo[3.3.1]nonane and 4,4,6-trimethyl-1,3,2-dioxaborinane is reviewed in the introductory part of Chapter IV. The monohydroboration of 1,2-cyclononadiene, 1,2-cyclodecadiene, 1,2-cyclotridecadiene, 3,4-octadiene and 2,4-dimethyl-2,3-pentadiene with catecholborane followed by oxidation resulted in the exclusive formation of the corresponding ketones due to the regioselective attack of boron at the central carbon atom of the allenic linkage. The monohydroboration of cyclic allenes followed by protonolysis with acetic acid gave the corresponding olefins in excellent yield. The formation of (Z)-cyclononene and (Z)-cyclodecene indicates the approach of the reagent from hydrogen side and ring side attack is not possible in the case of 1,2-cyclononadiene and 1,2-cyclodecadiene. In the case of 1,2-cyclotridecadiene the approach of the hydroborating agent is possible from hydrogen side as well as from ring side as evidenced by the formation of (Z)- and (E)-cyclotridecenes (76:24).

A brief summary of the syntheses of symmetrical (E,E)-1,3-dienes and reactions of organoboranes with silver nitrate forms the introductory part of Chapter V. trans-β-n-heptylethenylboronicacid with silver nitrate in presence of methanolic potassium hydroxide gave 1-nonene in 71% yield and the desired

(*E*,*E*)-8,10-octadecadiene in 24% yield. But, *trans*-β-phenylethenylboronicacid on similar reaction gave only styrene as the exclusive product. However, reaction of *trans*-β-phenylethenylboronicacid with bis(benzonitrile)palladium(II) chloride in presence of base gave the desired (*E*,*E*)-1,4-diphenyl-1,3-butadiene in excellent yield. On the other hand *trans*-β-*n*-heptylethenylboronicacid gave 1-nonene (14%) and a mixture of (*Z*,*Z*), (*Z*,*E*) and (*E*,*E*)-8,10-octadecadienes (76%) in the ratio of 3:30:67. *trans*-β-*p*-Methylphenylethenylboronicacid and *trans*-β-*p*-methoxyphenylethenylboronicacid on similar treatment gave the desired (*E*,*E*)-1,4-bis(*p*-methylphenyl)-1,3-butadiene and (*E*,*E*)-1,4-bis(*p*-methoxyphenyl)-1,3-butadiene respectively in excellent yield. We suggest that the reaction proceeds through dichlorodivinylpalladiumdianion to form the corresponding vinyl radicals, which in turn lead to the formation of various products. Thus, the present investigation provides an excellent method for the syntheses of (*E*,*E*)-1,4-diaryl-1,3-butadienes from arylacetylenes.

CHAPTER I

HYDROBORATION AND DIIMIDE REDUCTION OF CARYOPHYLLENE AND ISOCARYOPHYLLENE[1]

I.1 ABSTRACT

The monohydroboration of caryophyllene with dicyclohexylborane followed by oxidation causes the participation of the very highly reactive (E)-trisubstituted double bond in preference to the exocyclic double bond during hydroboration in an anti-Markovnikov's manner to give the corresponding unsaturated alcohol in a reasonable yield. This unsaturated alcohol from caryophyllene has been further transformed into the corresponding unsaturated ketone by oxidation using pyridinium chlorochromate in excellent yield. On the other hand, isocaryophyllene under similar conditions provides the corresponding unsaturated alcohol as the major product, wherein the participation of the least hindered exocyclic double bond takes place during hydroboration. Our attempts to achieve cyclic hydroboration with caryophyllene or isocaryophyllene using thexylborane resulted in the formation of the corresponding unsaturated alcohol instead of the expected diol. However, we have been able to achieve

regioselective reductions of caryophyllene and isocaryophyllene with diimide to produce the corresponding dihydroderivative in good yields. The structures of all these compounds have been established thoroughly by spectral and analytical data. Thus, the present procedures provide convenient methods of synthesizing these unsaturated alcohols and dihydrocaryophyllene in caryophyllene system for the first time.

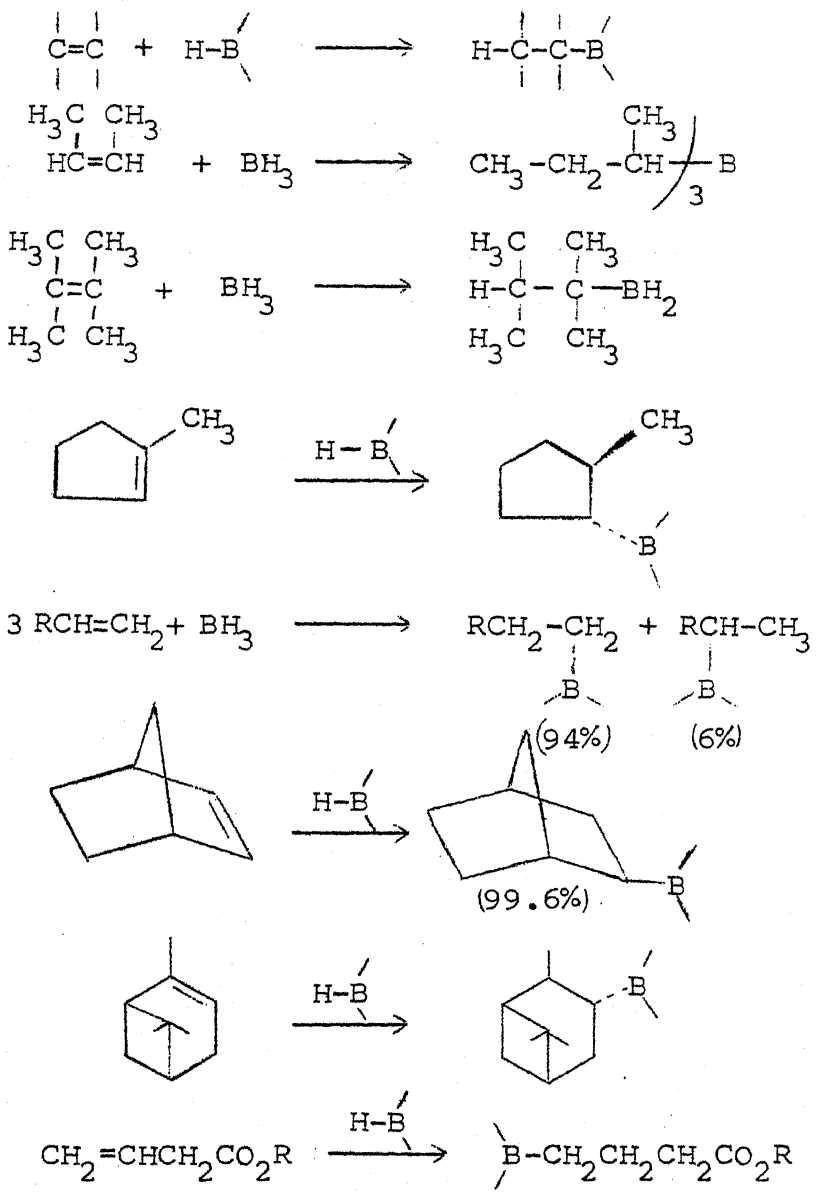
I.2 INTRODUCTION

The ready availability of organoboranes *via* hydroboration reaction and the diverse synthetically useful reactions exhibited by organoboranes have made them quite valuable reagents for synthetic applications. Reductions by sodium borohydride and lithium aluminiumhydride appear to involve a transfer of hydride ion from the anion to an electron-deficient center of the functional group.[2] BH_3 is a Lewis acid and reduction by BH_3 appears to involve a preferred electrophilic attack on the centre of highest electron density.[3] By a judicious use of diborane and alkali metal borohydrides, it has become possible to reduce many functional groups in the presence of other groups and to reverse the process at will.

Diborane reacts readily in ether solvents with olefins,[4] acetylenes[5] and dienes,[6] etc. The reaction is quantitative and practically instantaneous.[7] Practically all unsaturated compounds, even highly hindered olefins, react. The addition of $\rangle$B-H bond

is predominantly cis, anti-Markovnikov and takes place from the less hindered side of the double bond.[8,9] No rearrangements of the carbon skeleton have been observed except for benzylic, allylic and allenic derivatives. Many functional groups can tolerate this reaction[3] (Scheme I.1):

Scheme I.1



One of the most convenient procedures for achieving hydroboration is to add boron trifluoride etherate to a suspension of sodium borohydride in a solution of the unsaturated organic compound in tetrahydrofuran[10] (Scheme I.2):

Scheme I.2

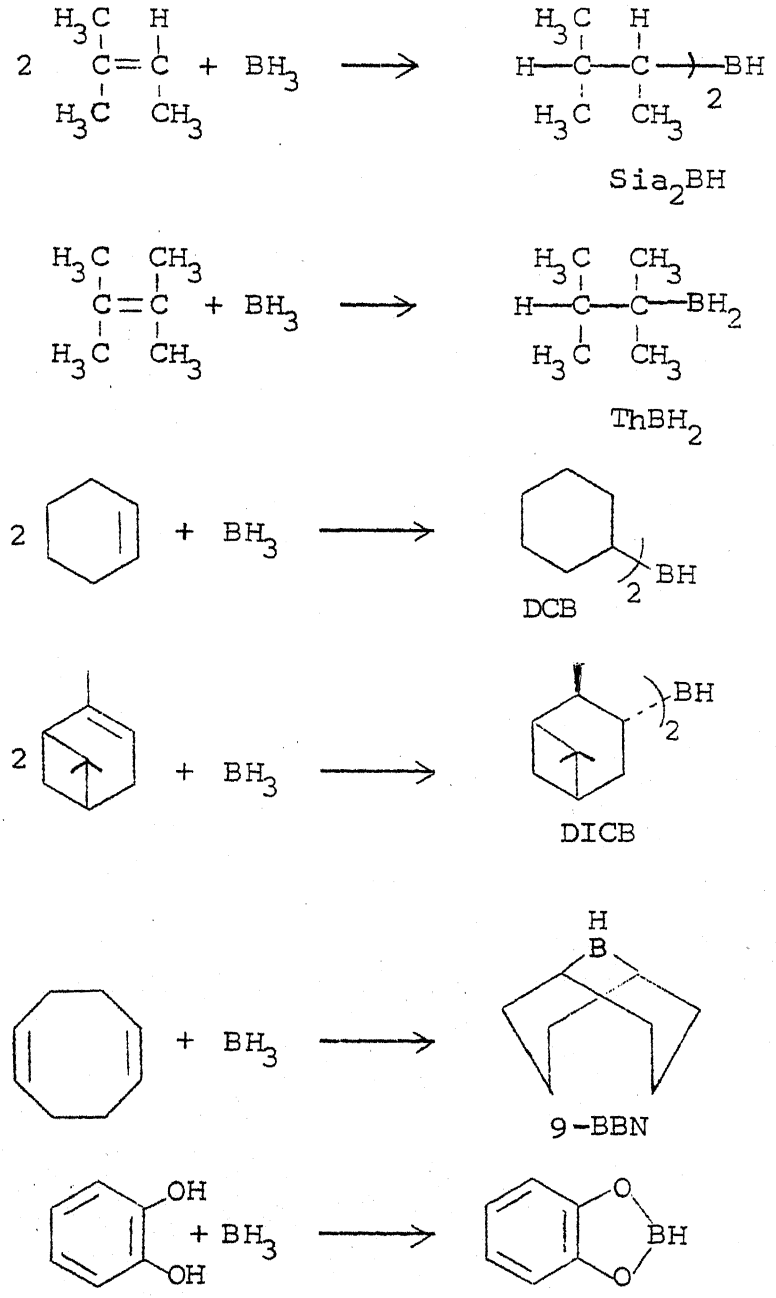
$$12\ RCH{=}CH_2 + 3\ NaBH_4 + 4\ BF_3{:}OEt_2 \xrightarrow[0^\circ]{THF} 4(RCH_2CH_2)_3B + 3\ NaBF_4 + 4\ Et_2O$$

Diborane is highly soluble in tetrahydrofuran and exists as addition compound, $H_3B{:}THF$.[11] This solution can be prepared readily,[12] and is now commercially available[13] ($BH_3{:}THF$ complex). The treatment of an unsaturated organic compound with a calculated quantity of standard $BH_3{:}THF$ solution constitutes the most convenient route to the synthesis of the corresponding organoborane. Another useful hydroborating agent is the complex of borane with dimethyl sulphide ($BH_3{:}SMe_2$) which is more stable than $BH_3{:}THF$.[14]

Hydroboration of simple olefins proceeds rapidly and quantitatively to the corresponding trialkylboranes. However, trisubstituted olefins such as 2-methyl-2-butene and tetrasubstituted olefins such as 2,3-dimethyl-2-butene rapidly react with borane to form dialkylborane, disiamylborane (Sia_2BH) and monoalkylborane; thexylborane ($ThBH_2$), respectively.[12] These partially alkylated organoboranes are the key intermediates,

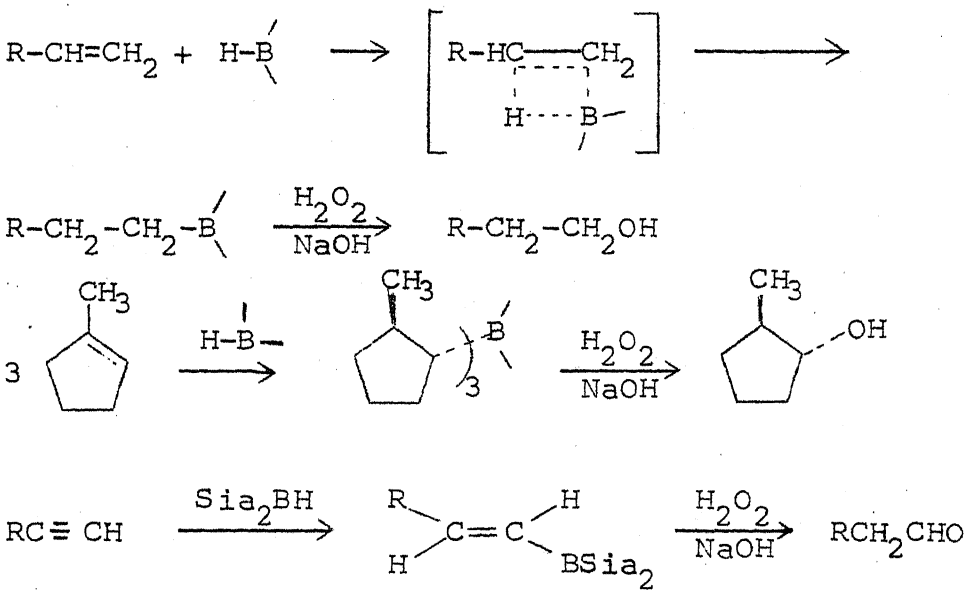
for the successful application of organoboranes in organic synthesis, as they provide a selective addition of boron-hydrogen bond to the unsaturated compounds. Other useful hydroborating agents include dicyclohexylborane (DCB) from cyclohexene, diisopionocamphenylborane (DICB) from α-pinene, 9-borabicyclo[3.3.1]-nonane (9-BBN) from Z,Z-1,5-cyclooctadiene and catecholborane[15] from catechol (Scheme I.3):

Scheme I.3



The hydroboration reaction involves a simple four-centered transition state with the direction of addition controlled both by electronic and steric factors. Oxidation of organoboranes with hydrogen peroxide in the presence of alkali is essentially quantitative and proceeds with retention of configuration. Consequently hydroboration followed by <u>in situ</u> oxidation with alkaline hydrogen peroxide provides a remarakbly simple and convenient procedure for the anti-Markovnikov hydration of double bond and triple bonds[15] (Scheme I.4):

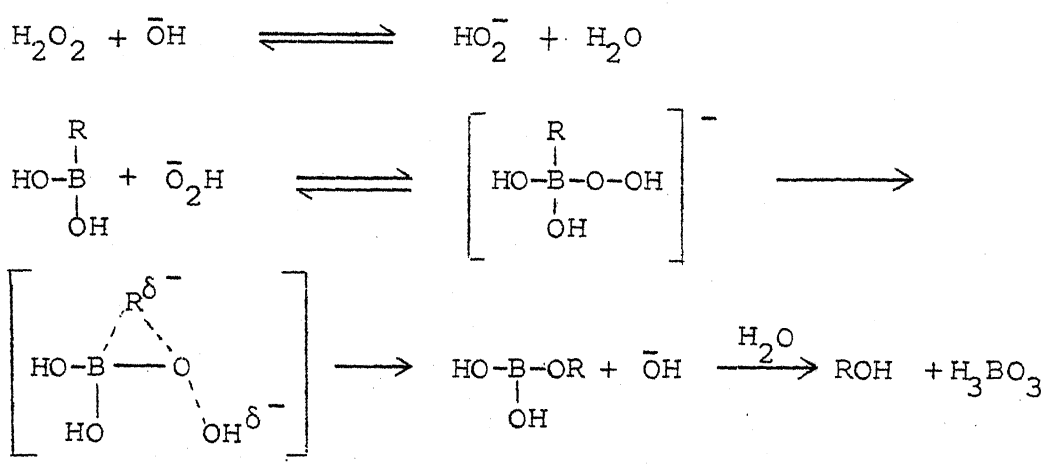
Scheme I.4



No detailed kinetic studies of the reaction with trialkylboranes have been reported. However, studies of the reaction of alkylboronic acids with alkaline hydrogen peroxide indicate that the reaction proceeds by an S_E2 mechanism. The following mechanism has been proposed for the base catalyzed reaction[16]

(Scheme I.5). An identical mechanism, in three sucessive stages, may be suggested for the oxidation of trialkylboranes, and is consistent with retention of configuration and free from rearrangements observed in the oxidation.

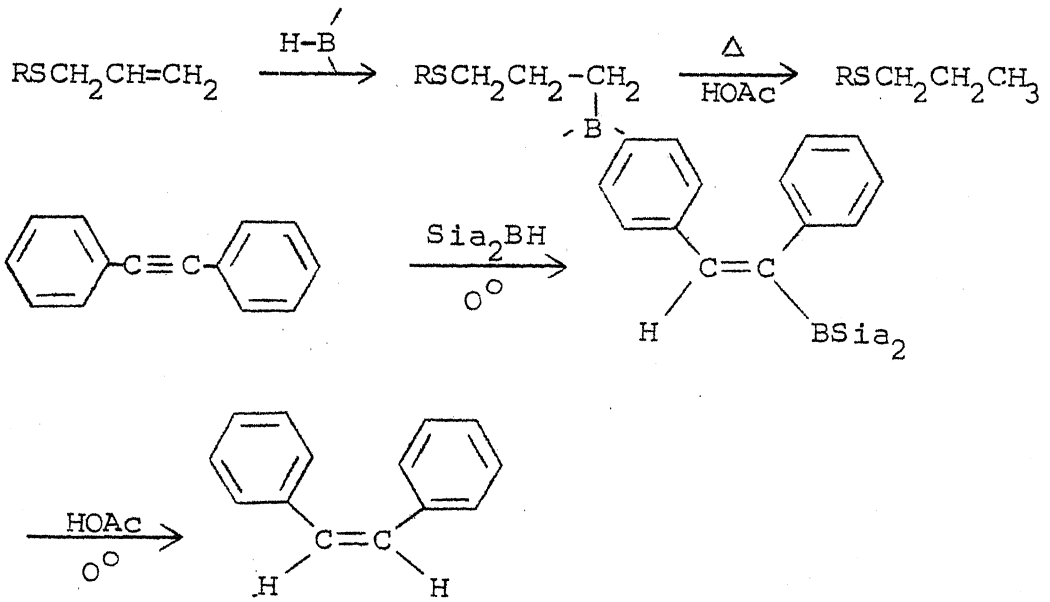
Scheme I.5



Alkylboranes are stable to water, aqueous mineral acids and aqueous alkalis but they are readily cleaved by carboxylic acids. This provides a convenient non-catalytic means of hydrogenating double bonds in compounds where the usual catalytic hydrogenation is difficult.[17] Vinylorganoboranes undergo protonolysis with particular ease providing a simple route to cis-olefins from acetylenes[18,19] (Scheme I.6).

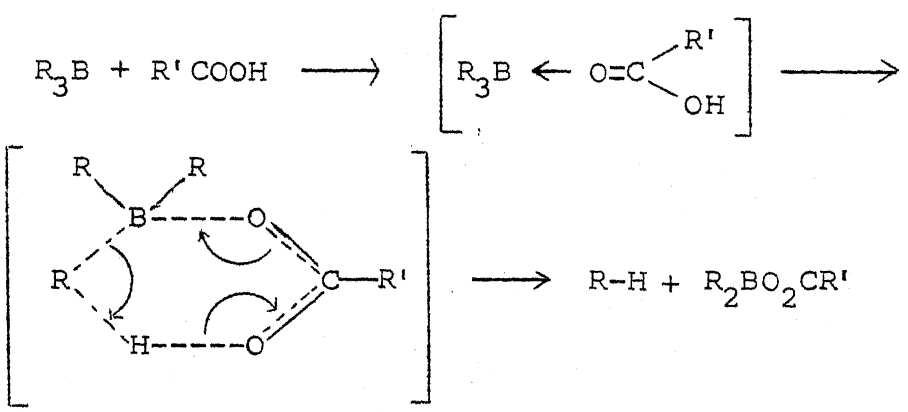
The mechanism of protonolysis involves prior coordination of the electrophilic boron to the carbonyl oxygen of the acid. This coordination process weakens the boron-carbon bond of the organoborane and increases the electrophilic character of the

Scheme I.6

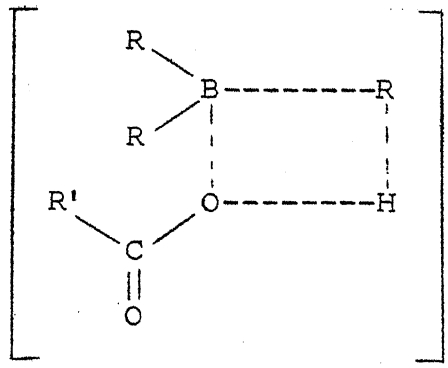


acidic hydrogen.[20] The rate determining proton transfer occurs via a six-membered transition state as shown in Scheme I.7:

Scheme I.7



As an alternative to cyclic six-membered transition state, a four-membered transition state has also been suggested.[21]



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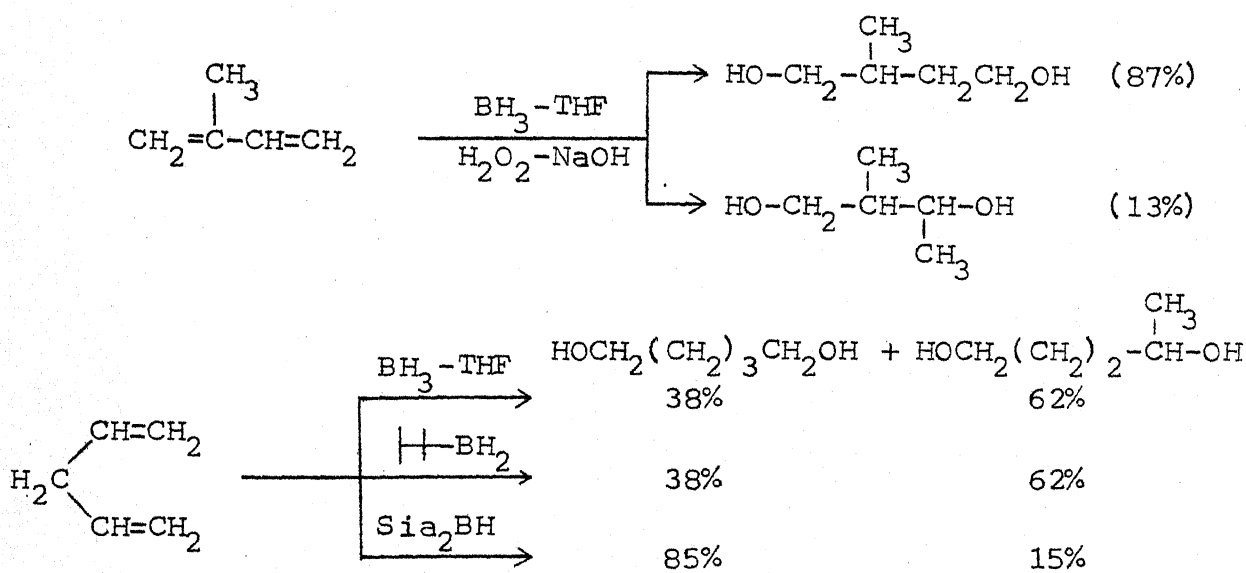
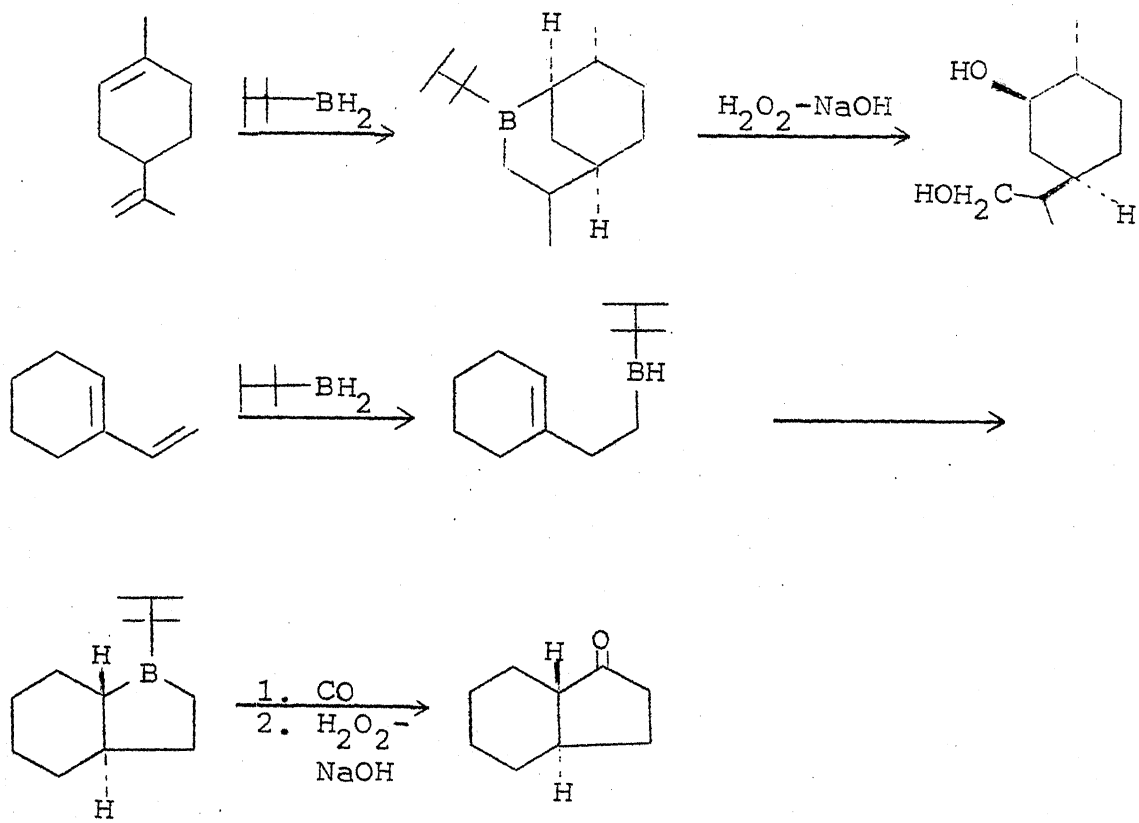
Hydroboration of a number of representative acyclic dienes (1,3-butadiene, substituted 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene) has been thoroughly investigated using borane,[6,22-25] thexylborane[26,27] and disiamylborane.[28,29] The intermediate organoboranes on oxidation with alkaline hydrogen peroxide yield isomeric diols. The distribution of the diols depends on the conditions of hydroboration and the nature of the olefin and hydroborating agent (Scheme I.8):

Scheme I.8

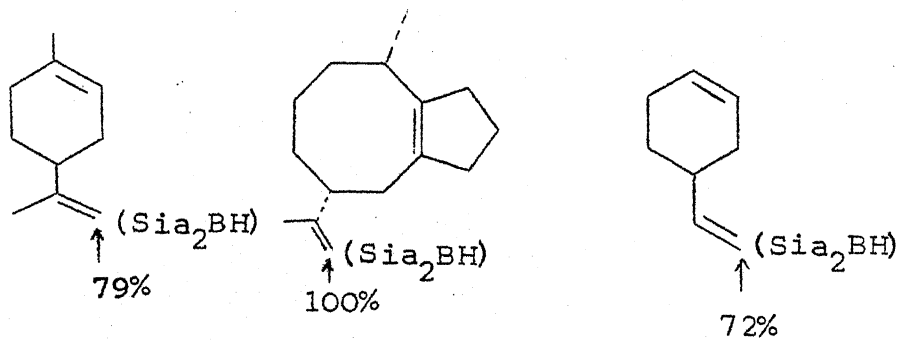


D(+)-Limonene[27] and vinylcyclohexene[30] undergo cyclic hydroboration with thexylborane to give bicyclic organoboranes which could be utilized either in the stereospecific synthesis of diols or bicyclic ketones (Scheme I.9):

Scheme I.9

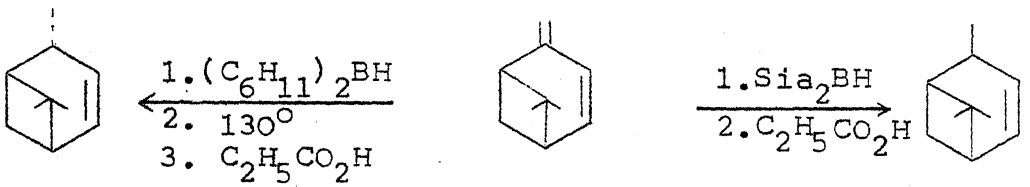


In the case of dienes containing one acyclic and one cyclic double bond the acyclic double bond usually undergoes selective hydroboration:[31-33]



Selective hydroboration of exocyclic double bond of verbenene has been used in the synthesis of cis and trans δ-pinene[33] (Scheme I.10):

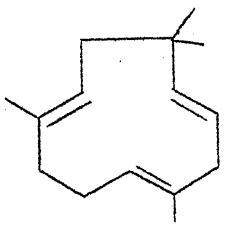
Scheme I.10



The chemistry of terpenoid compounds has long been an inspiration to the creative endeavors of the organic chemist. The field of study ranges through mono-, sesqui-, di- and triterpenoids and includes carotenoids and steroids. Apart from their intrinsic interest, terpenoid compounds have provided impetus for theoretical and mechanistic studies and for synthetic investigations. A sesquiterpenoid is a compound whose carbon skeleton can be theoretically constructed from three isoprenoid units. In the case of sesquiterpenoids the great majority of compounds can be regarded as built-up from the union of three isoprenoid residues joined head to tail order.

The sesquiterpene fraction of oil of cloves is the main source of caryophyllene. In older literature the terms α-, β -, γ-caryophyllene have been used to designate specific hydrocarbons from this source. Since α-caryophyllene is identical with humulene (1), it is now customary to call β-caryophyllene simply

as caryophyllene (2) and γ-caryophyllene as isocaryophyllene (3).



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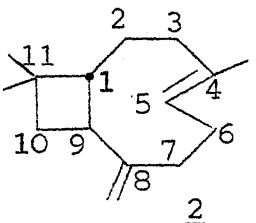

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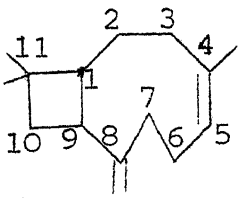
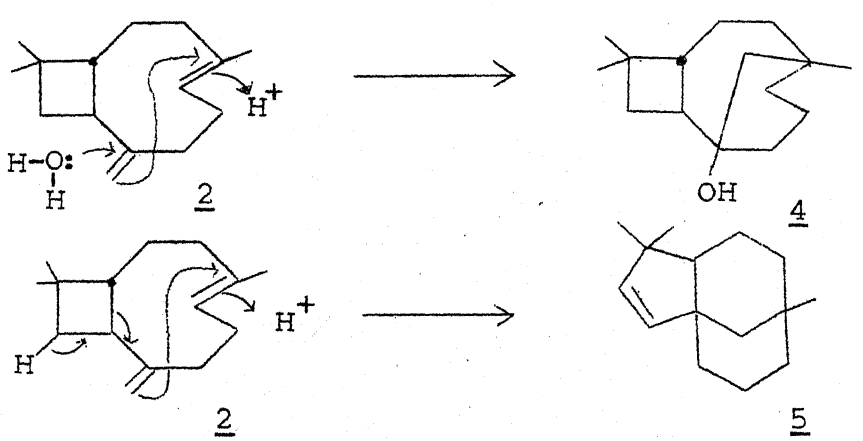


3

The unique structural features present in the isomeric sesquiterpenes, caryophyllene (2) and isocaryophyllene (3) made them a rich source of interesting reactions. The unusual structural features are the four- and nine-membered rings, the trans-ring junction which unites them, the presence of an endocyclic trisubstituted double bond in the nine-membered ring at proper location, with appropriate configuration and finally, the exocyclic methylene as shown in 2 and 3.[34]

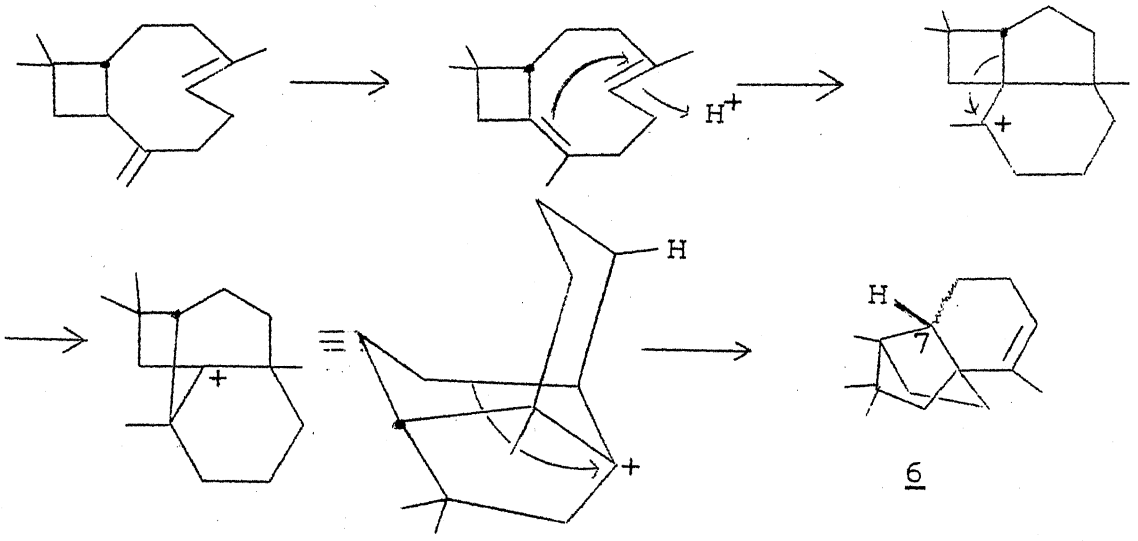
By the action of a number of acidic reagents caryophyllene may be cyclised to give a substance originally known as β-caryophyllene alcohol, but now termed as caryolan-1-ol (4) and clovene[35] (5) (Scheme I.11):

Scheme I.11



Reinvestigation of the sulphuric acid catalysed rearrangement of caryophyllene (2) by Parker revealed the presence of six hydrocarbons in the hydrocarbon fraction, comprising mainly clovene and an uncharacterized isomeric hydrocarbon designated as neoclovene (6).[36] Its formation has been explained in the Scheme I.12:

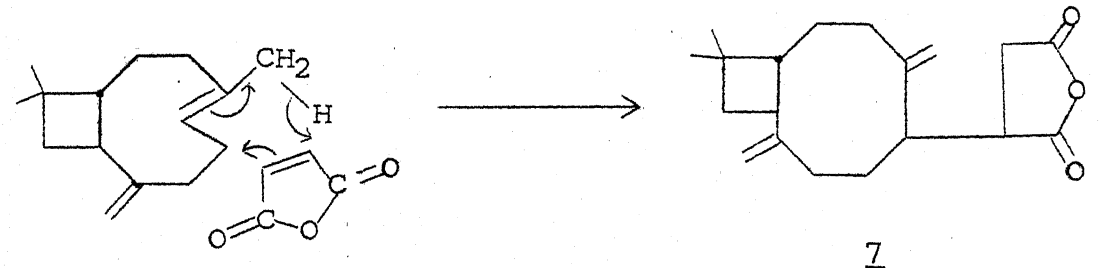
Scheme I.12



6

A particularly interesting reaction of caryophyllene is the formation of adduct 7 with maleic anhydride.[37] It is formed by attachment to an allylic system with migration of the double bond as illustrated in Scheme I.13:

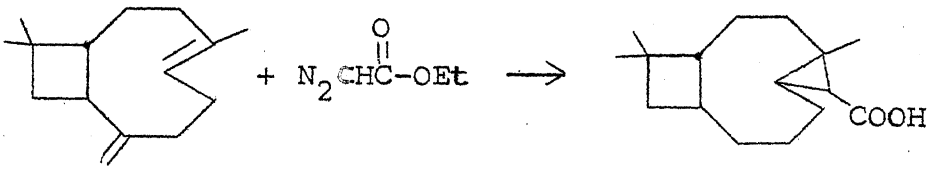
Scheme I.13



2 7

Addition of diazoaceticester to caryophyllene (2) at 170° in presence of copper followed by saponification gave the corresponding cyclopropane carboxylic acid (8) in 17% yield[38] (Scheme-I.14):

Scheme I.14

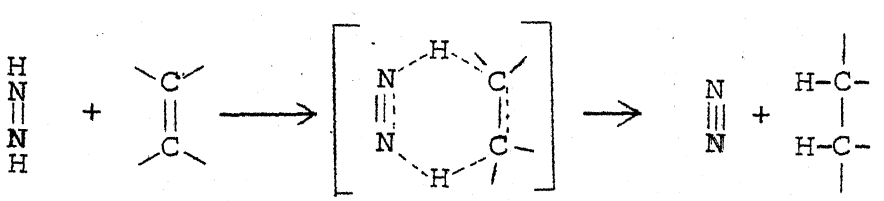


2 8

It is clear from these reactions that the trisubstituted double bond reacts in preference to the exocyclic double bond in caryophyllene system. Our interest in the chemistry of nine-membered cyclic system[39] prompted us to examine the behaviour of caryophyllene (2) and isocaryophyllene (3) towards diimide reduction and hydroboration[40] reactions.

Diimide reduces nonpolar carbon-carbon and nitrogen-nitrogen multiple bonds such as olefins, acetylenes and azocompounds. The mechanism of diimide reduction of a multiple bond is believed to involve a "synchronous transport" of hydrogen through a cyclic transition state[41,42] (Scheme I.15):

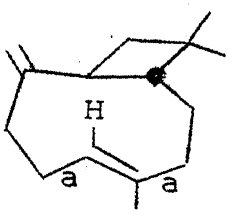
Scheme I.15



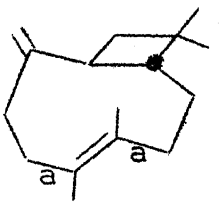
Diimide has been used for the selective reduction of allenes[43,44] and the (E) double bond of (Z,E)-1,5-cyclodecadiene.[45] Diimide possesses advantages over metal catalyzed hydrogenation. For example, diimide reduction gives no migration or cis-trans isomerization of double bonds when reduction is done in stages as is characteristic of catalytic processes.[46] On palladium-catalysed hemihydrogenation, isocaryophyllene gave dihydro-compound in which the excocyclic double bond has been reduced.[47] Under the same conditions caryophyllene also gave the same dihydro-compound. So it was concluded that the trans double bond has been isomerised to cis on palladium catalyst during hydrogenation.[47]

The molecular model of caryophyllene (2) indicates that the arrangement of nine-membered ring is perpendicular to the plane of the cyclobutane ring while the angular, torsional and steric strains are minimum. There are two such conformers (2A and 2B) in each of which only one face of the π-bond is exposed while the otherside being completely shielded by the rest of the molecule. However, the barrier to rotation of the trans double bond of caryophyllene (2A $\rightleftharpoons$ 2B) about the single bonds "a" could be higher than that of trans-cyclononene.[48] The trans fused cyclobutane ring and its attached exocyclic methylene group remove some of the freedom of rotation in the cyclononene ring of caryophyllene. Since interconversion of 2A and 2B must occur by movement of one substituent on the double bond through the "hole" in the nine-membered ring, the probability of 180° rotation about bonds "a"

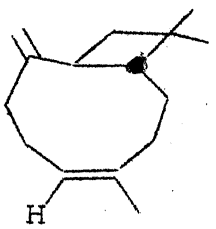
in 2A or 2B relative to the same rotation in trans-cyclononene will be halved by the presence of allylic methyl group which



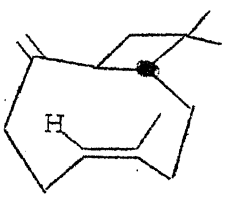
2A



2B



3A



3B

cannot pass through the "hole". Nickon et al. have explained the formation of clovene and caryolan-1-ol from the two distinctly different conformations 2A and 2B respectively.[49] Hence, cis-addition of symmetrical reagent to this carbon-carbon double bond, can give only one diastereomer from each conformer. Isocaryophyllene (3) is more flexible and the conformers 3A and 3B are easily interconvertible and both sides of the double bond are relatively accessible for attack by symmetrical reagents. Hence one could expect no or little stereospecificity.[50] The disposition of the exocyclic double bond in caryophyllene conformers (2A and 2B) suggests that the α-side (i.e., syn to the angular hydrogen next to the gem-dimethyl unit) provides a less crowded environment for the double bond. Hence the approach of any reagent with steric requirements should be preferred from this side. On the other hand, the molecular models of isocaryophyllene conformers 3A and

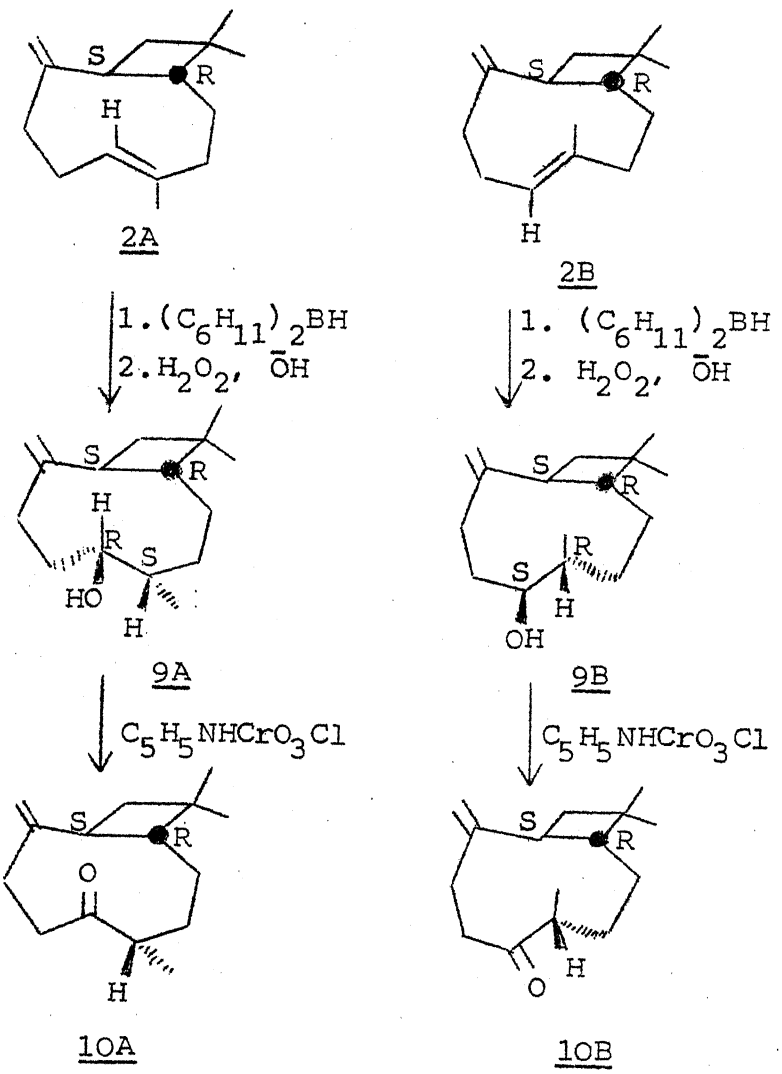
3B indicate equal accessibility to both sides of the exocyclic double bond as compared to 2A and 2B.

The above examination of caryophyllene (2) and isocaryophyllene (3) prompted us to study the selectivity of monohydroboration reaction and diimide reduction. Since there are two different unsaturation sites with different disposition in 2 and 3 making us possible to understand their intimate structural features and chemical reactivity in new direction. In the course of the study we were also interested to establish the participation of stable conformers 2A and 2B towards hydroboration and also trans-annular participation of both the double bonds in 2 and 3 towards cyclic hydroboration.

I.3 RESULTS AND DISCUSSION

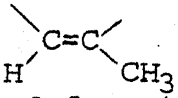
Monohydroboration of caryophyllene (2) with dicyclohexylborane[51] was studied varying the ratio of reactants in tetrahydrofuran in order to find optimum conditions for the formation of maximum quantity of monohydroboration product. When dicyclohexylborane and caryophyllene [(E)-(1R,9S)-4,11,11-trimethyl-8-methylenebicyclo(7.2.0) undecan-4-ene] (2) were used in a 2:1 molar ratio, the amount of recovered caryophyllene (2) was minimum and the yield of caryophyllene alcohol [(1R,9S)-4,11,11-trimethyl-8-methylenebicyclo(7.2.0)undecan-5-ol] (9) was maximum (70% yield), after the usual alkaline oxidation of the intermediate organoborane (Scheme I.16). The IR and NMR clearly support the product to be [(1R,9S)-4,11,11-trimethyl-8-methylenebicyclo(7.2.0)-

Scheme I.16

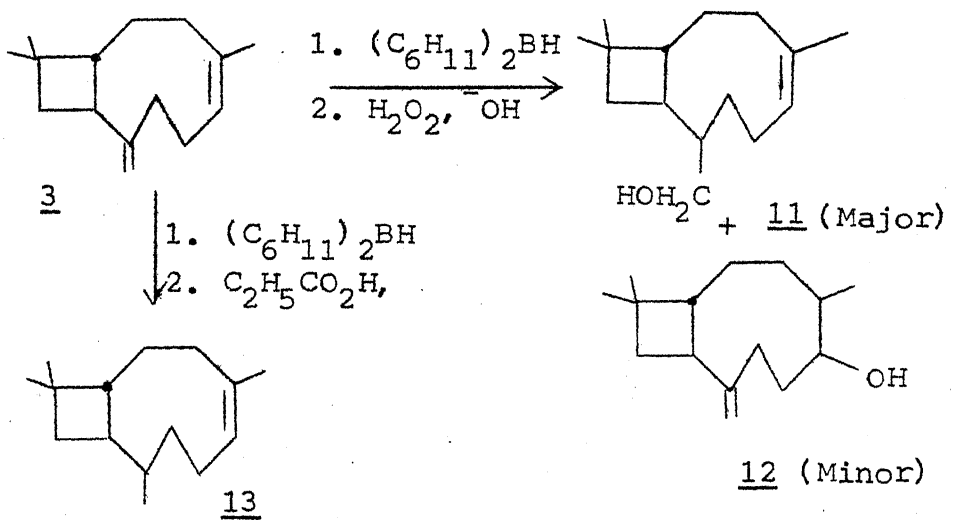


undecan-5-ol](9). Its IR spectrum showed the O-H stretching at 3625 and 3400 cm^{-1}, =C-H stretching at 3080 cm^{-1}, $C=CH_2$ stretching at 1640 cm^{-1} and $=CH_2$ out-of-plane deformation at 885 cm^{-1}, characteristic of the exocyclic methylene group. Furthermore the complete absence of a trisubstituted double bond is evident from the absence of its $\begin{matrix} H \\ \diagdown \\ C=C \\ \diagup \\ CH_3 \end{matrix}$ stretching at 1679 cm^{-1} and $=CH(CH_3)$ out of plane deformation at 835 cm^{-1}. The NMR spectrum of 9 showed the presence of hydroxyl proton at 2.17δ as a singlet and

vinyl methylene protons at 4.87 δ as a singlet. Oxidation of caryophyllene alcohol (9) with pyridinium chlorochromate,[52] provided caryophyllene ketone [(1R,9S)-4,11,11-trimethyl-8-methylenebicyclo(7.2.0)undecan-5-one] (10) in 72% yield. Its IR spectrum showed C=O stretching at 1715 cm^{-1}. The NMR spectrum showed two singlets at 4.95 δ and 4.85 δ for vinyl methylene protons. The DNP derivative melted in the range 190-198°. Our attempt to achieve cyclic hydroboration of caryophyllene (2) with thexylborane[53] resulted in the formation of only caryophyllene alcohol (9) after the usual alkaline hydrogen peroxide oxidation.

The hydroboration-oxidation of isocaryophyllene [(Z)-(1R,9S)-4,11,11-trimethyl-8-methylenebicyclo(7.2.0)undecan-4-ene] (3) with dicyclohexylborane yielded a mixture of isocaryophyllene alcohols [(Z)-(1R,9S)-4,11,11-trimethyl-8-hydroxymethylbicyclo-(7.2.0)undecan-4-ene] (11) and [(1R,9S)-4,11,11-trimethyl-8-methylenebicyclo(7.2.0)undecan-5-ol] (12) (70% yield) in a ratio of 4:1 as analysed by NMR spectrum of the product mixture (Scheme-I.17). However, isocaryophyllene alcohol (11) was obtained as the sole product by hydroboration of isocaryophyllene (3) with thexyl-borane[53] followed by alkaline hydrogen peroxide oxidation. The structure of 11 was readily determined by spectral data. Its IR spectrum showed O-H stretching absorptions at 3650 cm^{-1} and 3400 cm^{-1},  stretching frequency at 1670 cm^{-1} and  out-of-plane deformation at 840 cm^{-1}. The NMR spectrum displays an olefinic proton at 5.0-5.58δas a triplet (J = 6.5 Hz) and the hydroxyl proton at 2.17 δ as a singlet. Hydroboration of

Scheme I.17

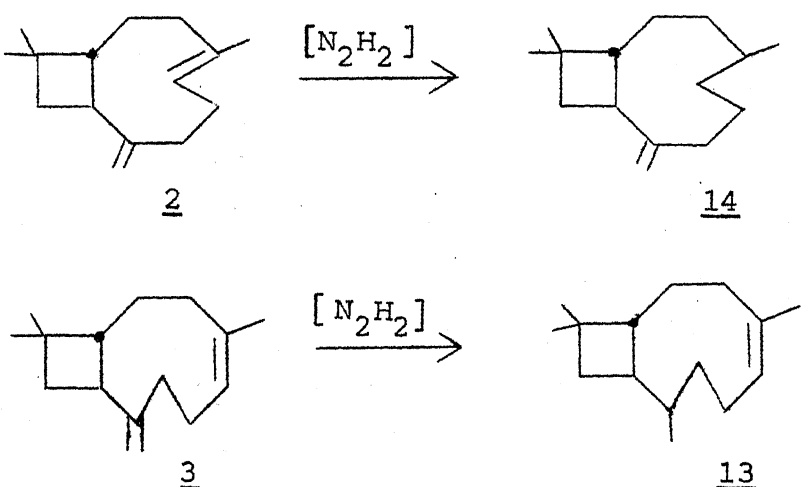


isocaryophyllene (3) with dicyclohexylborane followed by protonolysis[27] with propanoic acid yielded dihydroisocaryophyllene [(Z)(1R,9S)-4,8,11,11-tetramethylbicyclo(7.2.0)undecan-4-ene] (13) in 57% yield (Scheme I.17). The structure of 13 was deduced from its spectral characteristics. The IR spectrum of 13 showed $H\diagdown C{=}C\diagup CH_3$ stretching at 1670 cm^{-1} and a weak $\diagdown C{=}C\diagup H$ out-of-plane deformation at 835 cm^{-1}. The NMR spectrum of 13 shows an olefinic proton at 5.0-5.5 δ as a triplet (J = 7.5 Hz).

The reducing agent diimide was generated *in situ* by the oxidation of hydrazine with hydrogen peroxide in presence of cupric ions.[54,55] Partial reduction of caryophyllene (2) yielded dihydrocaryophyllene, [(1R,9S)-4,11,11-trimethyl-8-methylene-bicyclo(7.2.0)undecane] (14) in 87% yield. This was readily identified by its IR and NMR spectra. IR spectrum showed the presence of an exocyclic methylene at 3065, 1640 and 885 cm^{-1}. The NMR spectrum displayed two olefinic protons at 4.85 δ as a

singlet. Isocaryophyllene under similar conditions underwent conversion only to the extent of 80% to give dihydroisocaryophyllene (13) (Scheme I.18) which was separated by preparative gas-chromatography. The product was identified as 13 by comparing IR, NMR and gas chromatographic retention times with that of the sample obtained by hydroboration and protonolysis of isocaryophyllene (3).

Scheme I.18



2 14

3 13

Our results on the monohydroboration-oxidation of caryophyllene (2) conclusively point out that the more substituted (E)-double bond selectively participates during hydroboration to give satisfactory yield of the unsaturated alcohol namely caryophyllene alcohol (9). The selectivity as well as reactivity may be attributed to the strain in the (E)-double bond in a nine-membered ring[39] which is in agreement with the result of Brown.[40] Our experiments on the variation of molar ratio of caryophyllene 2 to dicyclohexylborane from 1:1 to 1:2 indicated the increase in the

conversion of 2. There was no contamination of the dihydroborated product inspite of the presence of 100% excess of dicyclohexylborane indicating the greater selectivity of the (E)-double bond over exocyclic double bond during hydroboration. This new unsaturated alcohol (9) on oxidation with pyridinium chlorochromate[52] gave the unsaturated ketone (10). The DNP derivative of (10) showed a large range in melting point even after recrystallisation indicating the presence of two diasteromeric ketones (10A and 10B). Furthermore, the NMR spectrum of 10 shows the presence of olefinic protons as two singlets at 4.85 δ and 4.95 δ in the ratio of 1:3, which may be due to the presence of two diastereoisomers (10A and 10B). Our attempts to separate the two diastereoisomers (10A and 10B) have been futile. It has been shown that caryophyllene (2) forms two (E)-epoxides on peracid epoxidation[50] and hence the presence of two conformers (2A and 2B). Since the addition of B-H is cis, occurs from the less hindered side and replacement of boron by hydroxyl in the oxidation proceeds with retention of configuration,[12] one would expect the formation of two diastereoisomeric unsaturated alcohols 9A [(1R,4S,5R,9S)-4,11,11-trimethyl-8-methylenebicyclo(7.2.0)undecan-5-ol] and 9B [(1R,4R,5S,9S)-4,11,11-trimethyl-8-methylenebicyclo-(7.2.0)undecan-5-ol], only when both the conformers of caryophyllene (9A and 9B) participate in the hydroboration reaction. Therefore, our results are in agreement with the findings of Warnhoff and Srinivasan.[50] Our attempts to achieve protonolysis of the intermediate organoborane from 2 resulted in the formation of a complex mixture of products as shown by GLC analysis and

therefore, no attempt was made to separate and characterise each of these products. This may be attributed to the instability of the organoborane towards protonolytic conditions. Our attempt to achieve cyclic hydroboration of 2 using thexylborane is not successful and gave unsaturated alcohol on oxidation. This suggests that, the B-H bond in the intermediate unsaturated organoborane is not suitably disposed for a transannular addition across the nine-membered ring.

The hydroboration of isocaryophyllene (3) with dicyclohexylborane followed by oxidation gave a mixture of unsaturated alcohols 11 and 12 in a ratio of 4:1. Although the reaction is less selective, the formation of 11 as the major product indicates greater selectivity of dicyclohexylborane at the disubstituted exocyclic double bond over endocyclic (Z)-trisubstituted double bond. However, we have been able to achieve complete selectivity using thexylborane during our attempts to achieve cyclic hydroboration which yielded the unsaturated alcohol (11) as the sole product. The spectral data of 11 is not adequate to determine the configuration at C-8, protonolysis of the mixture of intermediate organoboranes by treating isocaryophyllene (3) with dicyclohexylborane gave the dihydroisocaryophyllene (13) as the only product. This is attributed to the facile reactivity of a primary carbon-boron bond towards protonolysis reactions, compared to a secondary carbon-boron bond.[27]

Caryophyllene (2) when treated with diimide gave the 4,5-dihydroderivative. The selectivity observed may be attributed to

the strain of the (E)-trisubstituted double bond in the nine-membered ring. However, in the case of isocaryophyllene the exo-double bond is selectively reduced as the trisubstituted double bond is more crowded and has no strain. These results are in concurrence with the observed partial reduction of (Z,E)-1,5-cyclodecadiene[45] and terminal allenes.[43,44]

The results of this study fully support the earlier generalizations regarding the selectivity of the monohydroboration reaction and partial diimide reduction of dienes in which the two double bonds differ either in substitution and/or configuration. Oxidation of the unsaturated alcohol (9) to the unsaturated ketone (10) further establishes the presence of two conformers (2A and 2B) of caryophyllene (2). The present procedures provide convenient methods of preparing caryophyllene alcohol (9), caryophyllene ketone (10) isocaryophyllene alcohol (11) and dihydrocaryophyllene (14) for the first time.

I.4 EXPERIMENTAL

The boiling points are uncorrected. All IR spectra were recorded on a Beckman IR-8 spectrometer in CCl_4 solvent. The NMR spectra were recorded on Bruker WH-90 spectrometer, in deuterochloroform using tetramethylsilane as an internal standard. GLC analysis was done on a Varian Aerograph Model 90-P Instrument, on 15% silicone rubber 5'x$\frac{1}{4}$" and 20% carbowax 20 M 15'x$\frac{1}{4}$" (F & M

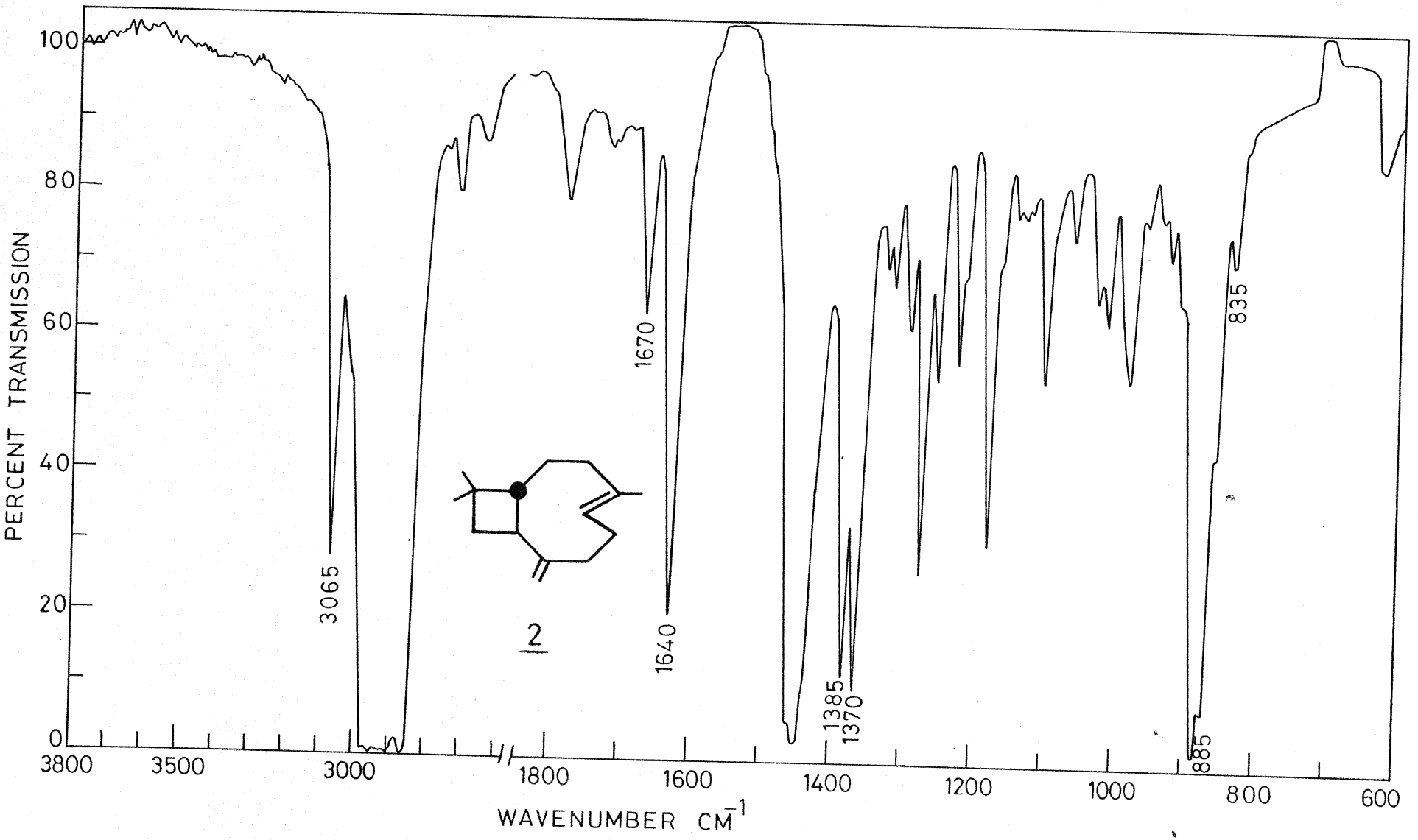
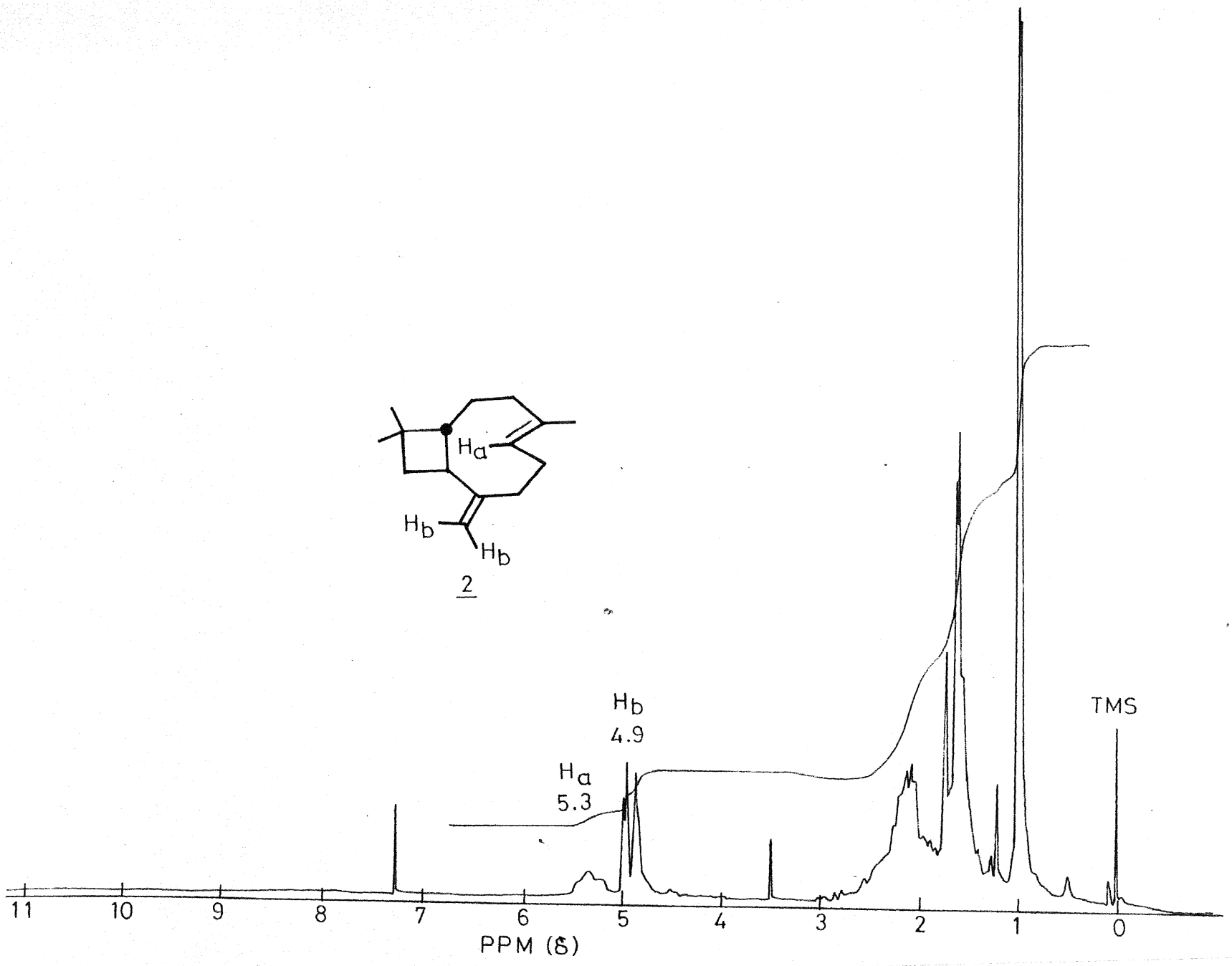


Fig. 1.1 IR spectrum of caryophyllene (2).


Ha
Hb
Hb
2
Hb
4.9
Ha
5.3
TMS
11
10
9
8
7
6
5
4
3
2
1
0
PPM (δ)

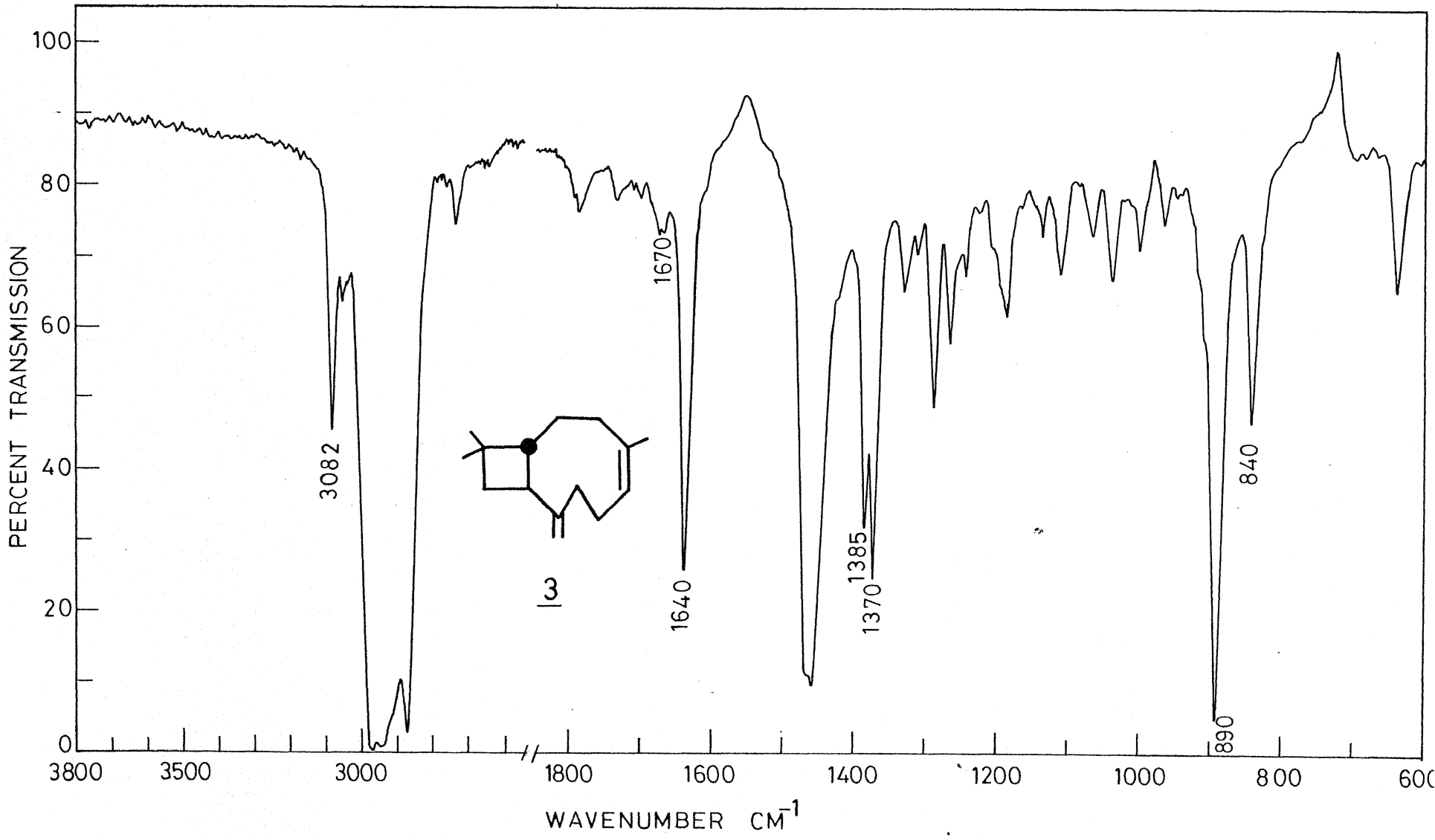


Fig. 1.3 IR spectrum of isocaryophyllene (3).

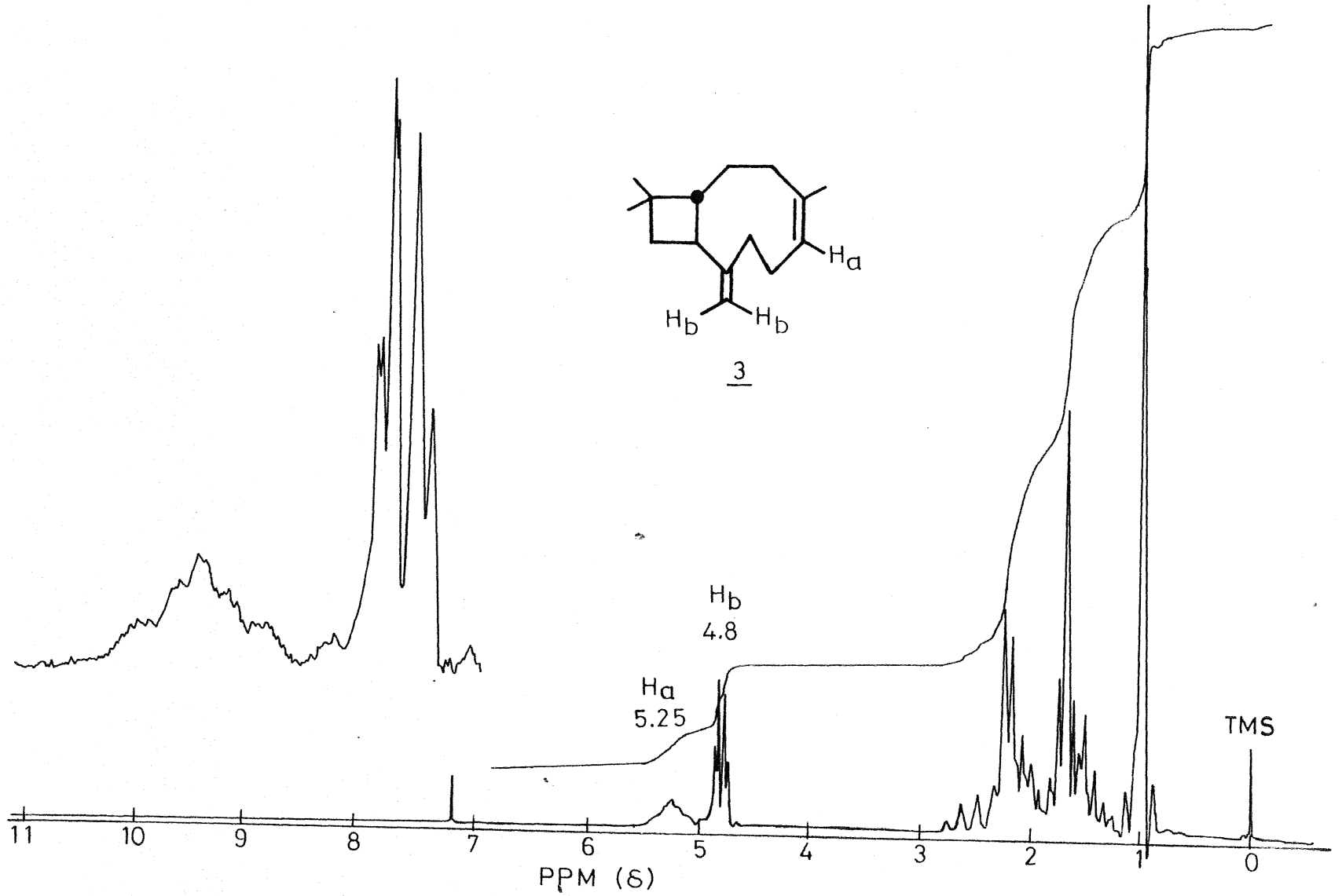


Fig. 1.4 NMR spectrum of isocaryophyllene (3).

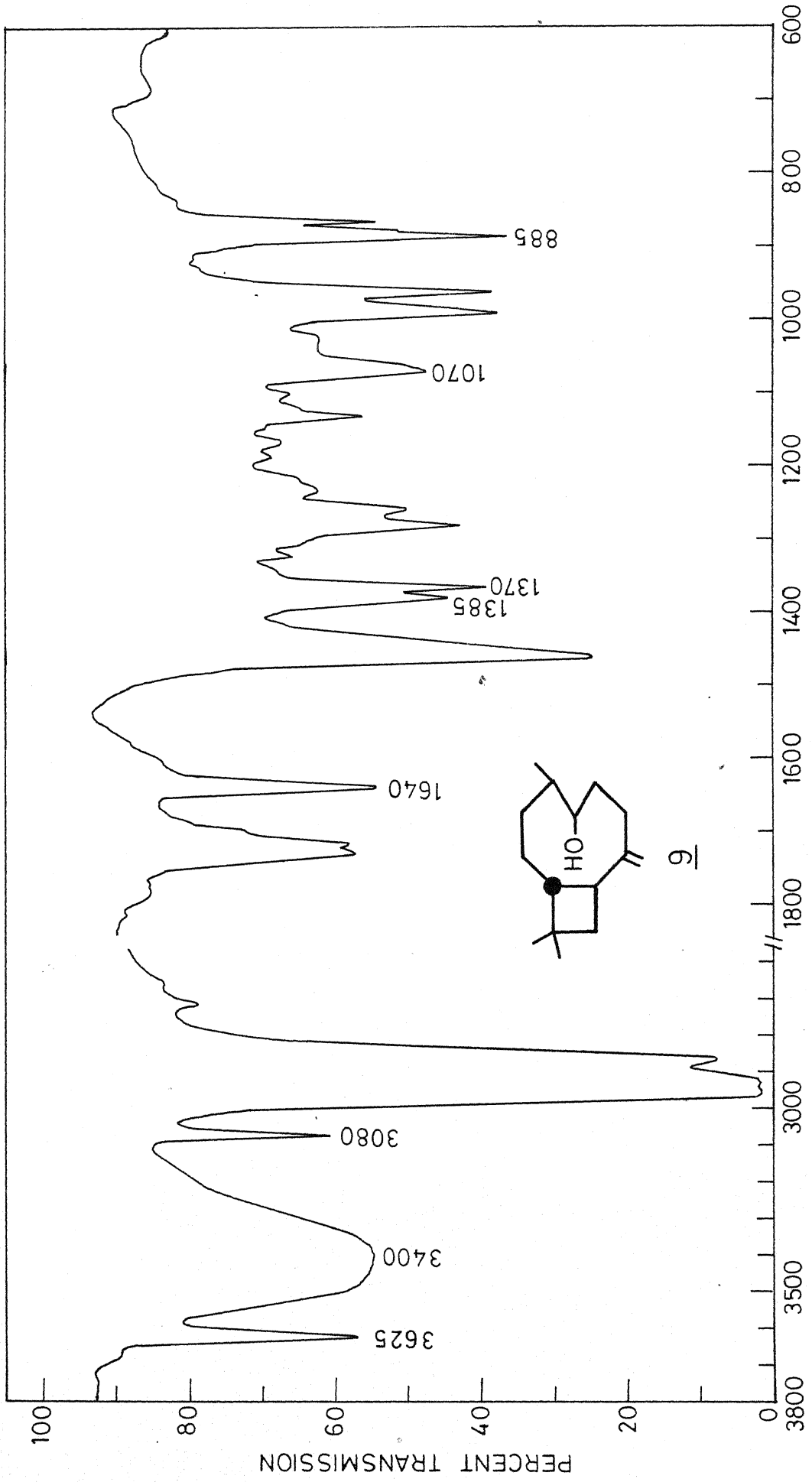


Fig. 1.5 IR spectrum of caryophyllene alcohol (9).

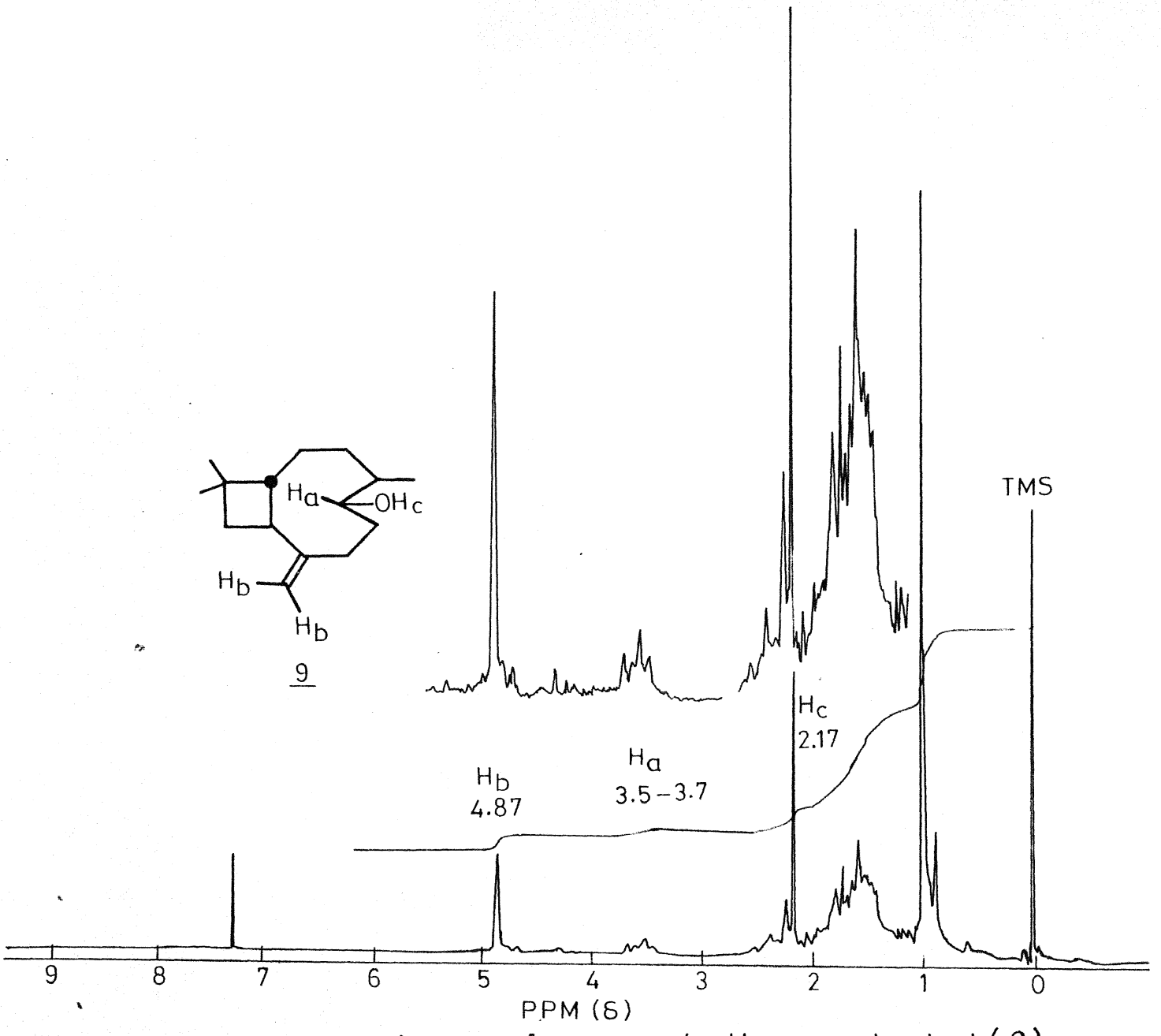


Fig. 1.6 NMR spectrum of caryophyllene alcohol (9).

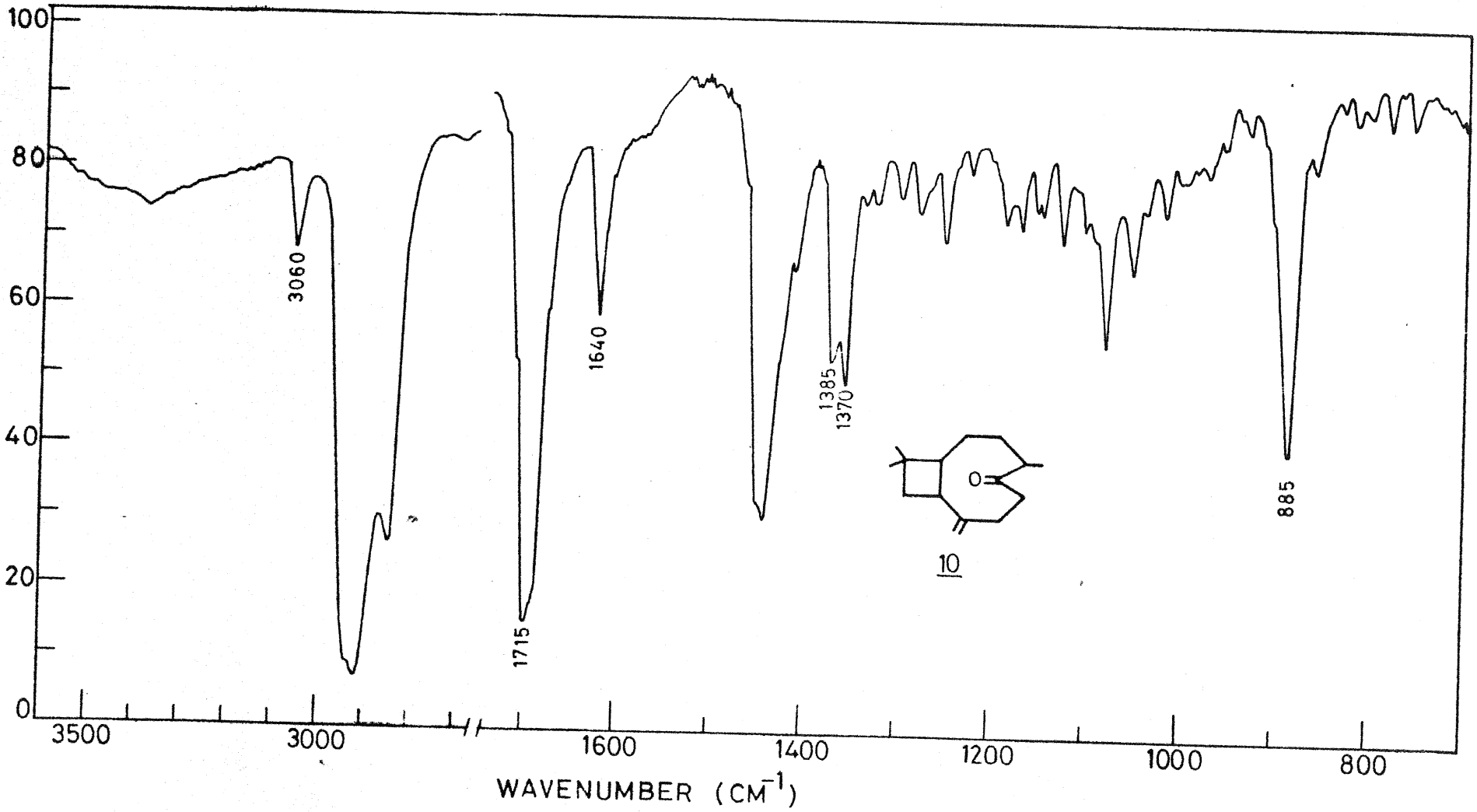


Fig. 1.7 IR spectrum of caryophyllene ketone (10).

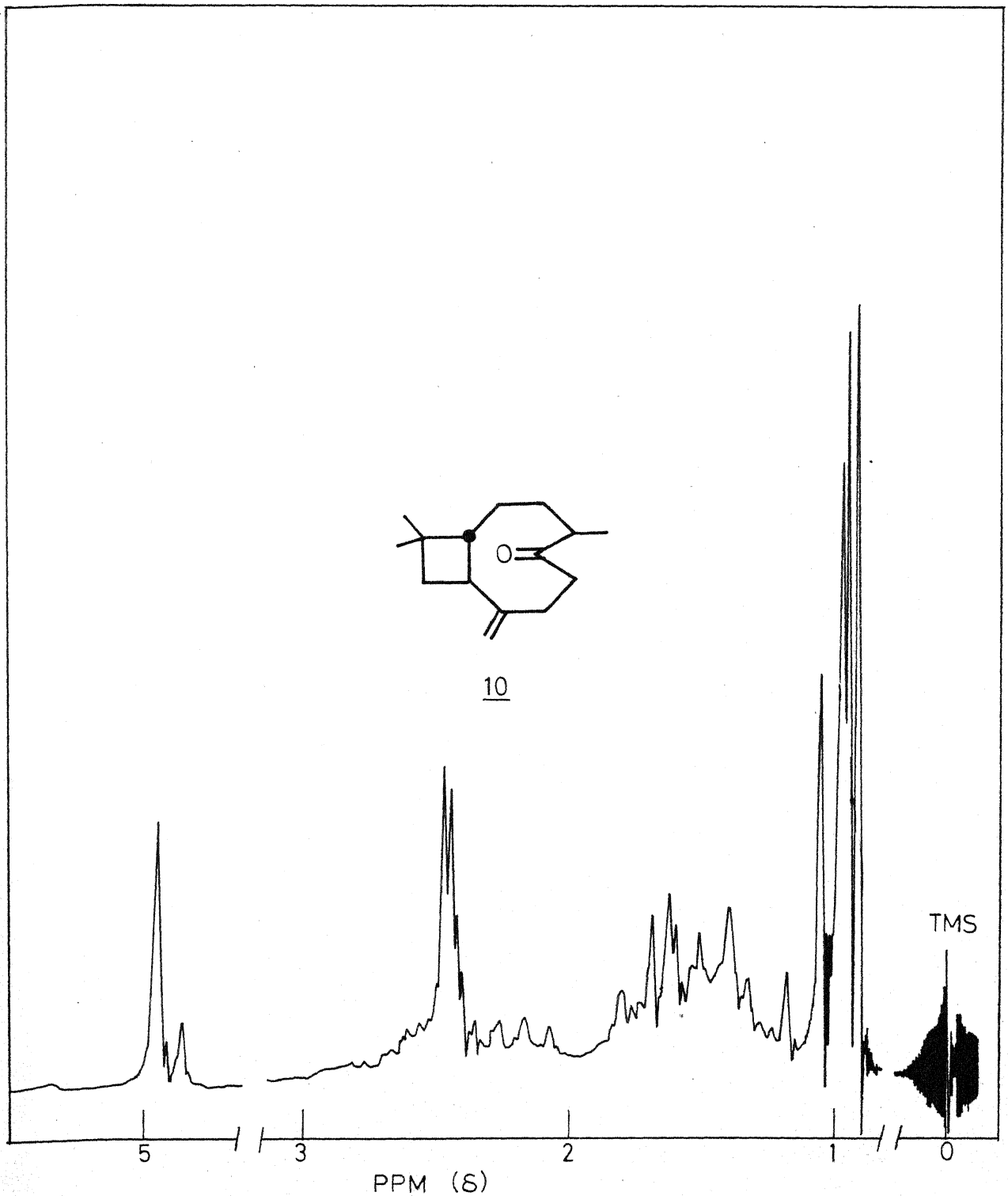


Fig. 1.8 NMR spectrum of caryophyllene ketone(10).

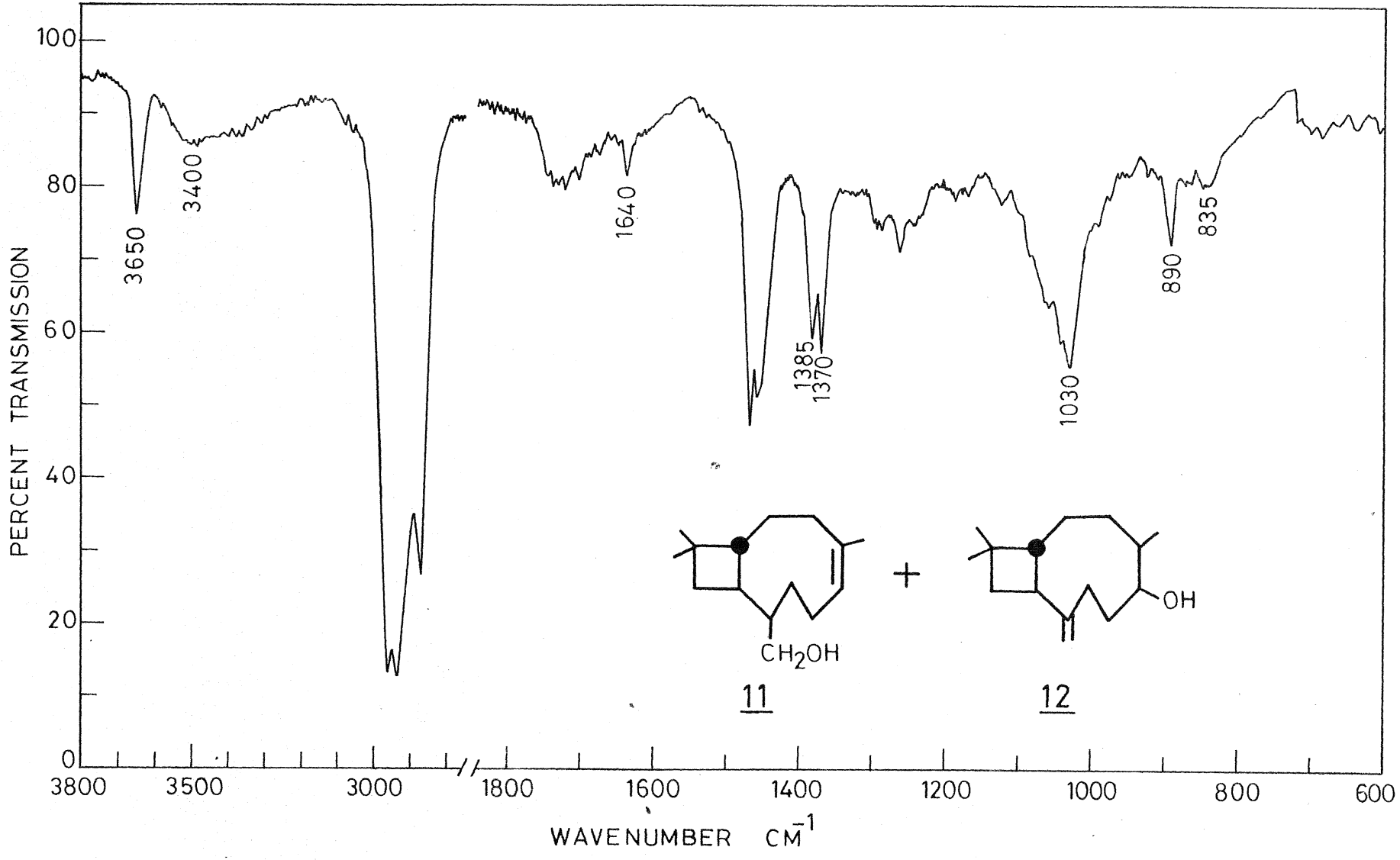


Fig. 1.9 IR spectrum of isocaryophyllene alcohols (11+12).

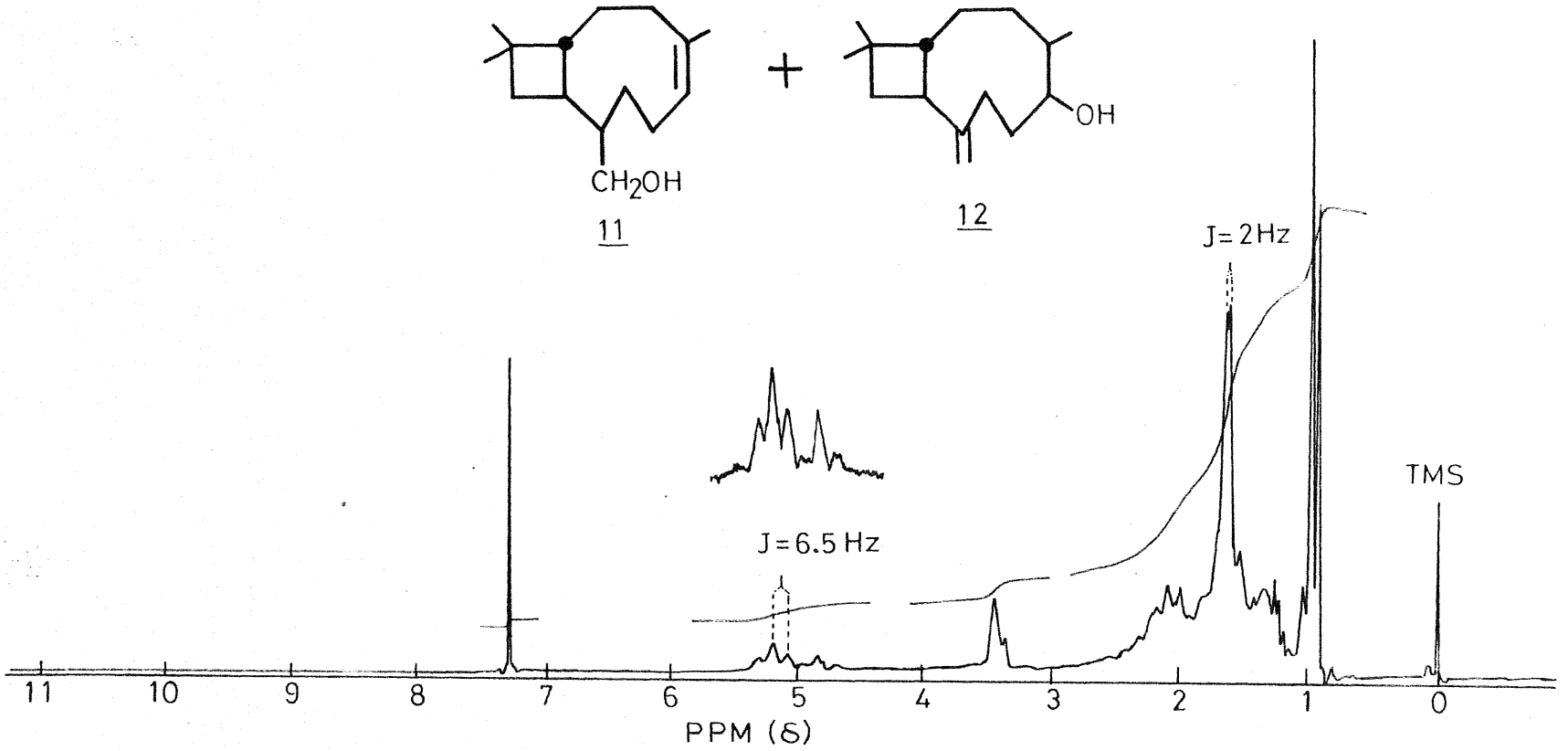


Fig. 1.10 NMR spectrum of isocaryophyllene alcohols (11+12).

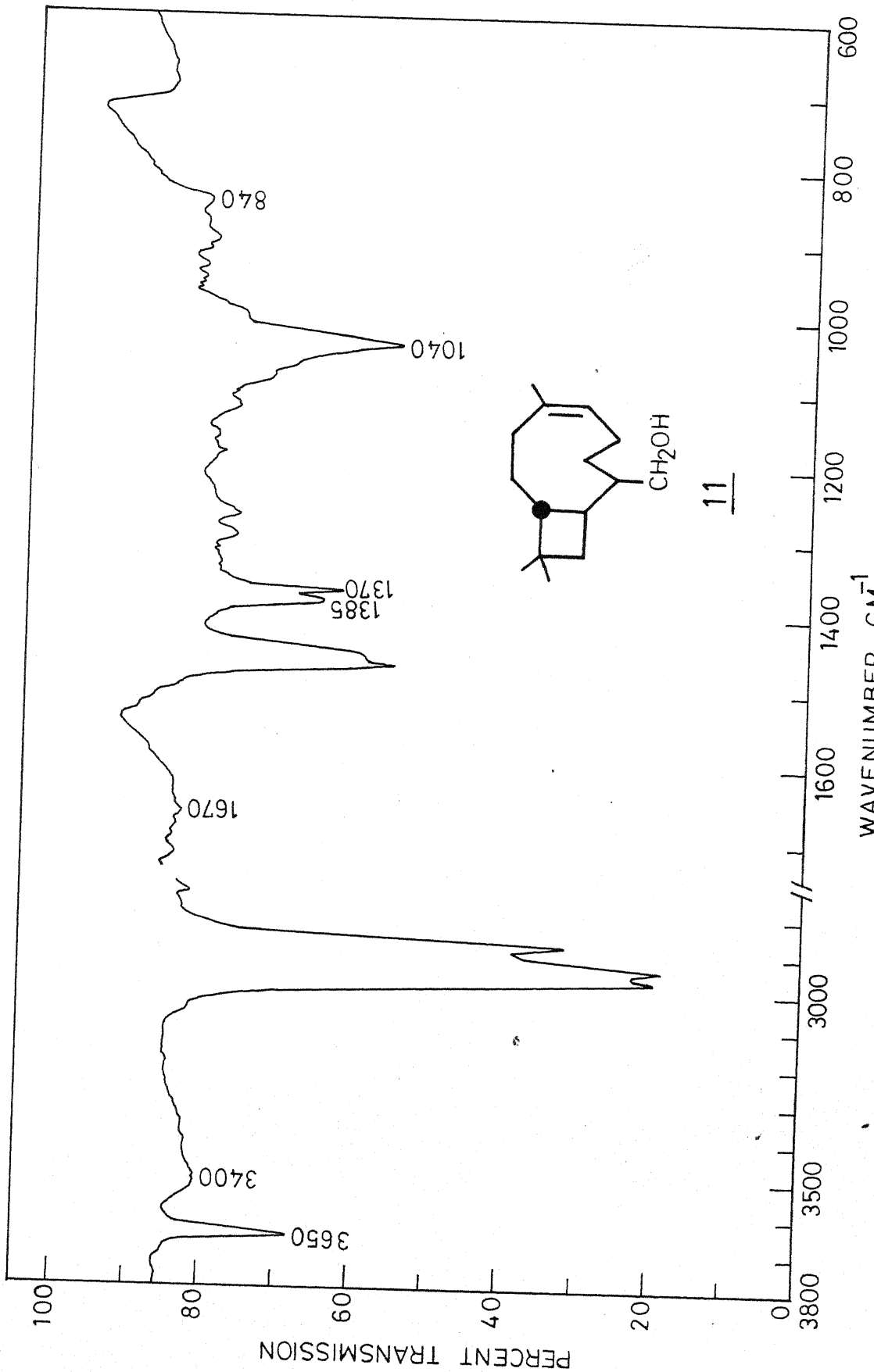


Fig. 1.11 IR spectrum of isocaryophyllene alcohol(11).

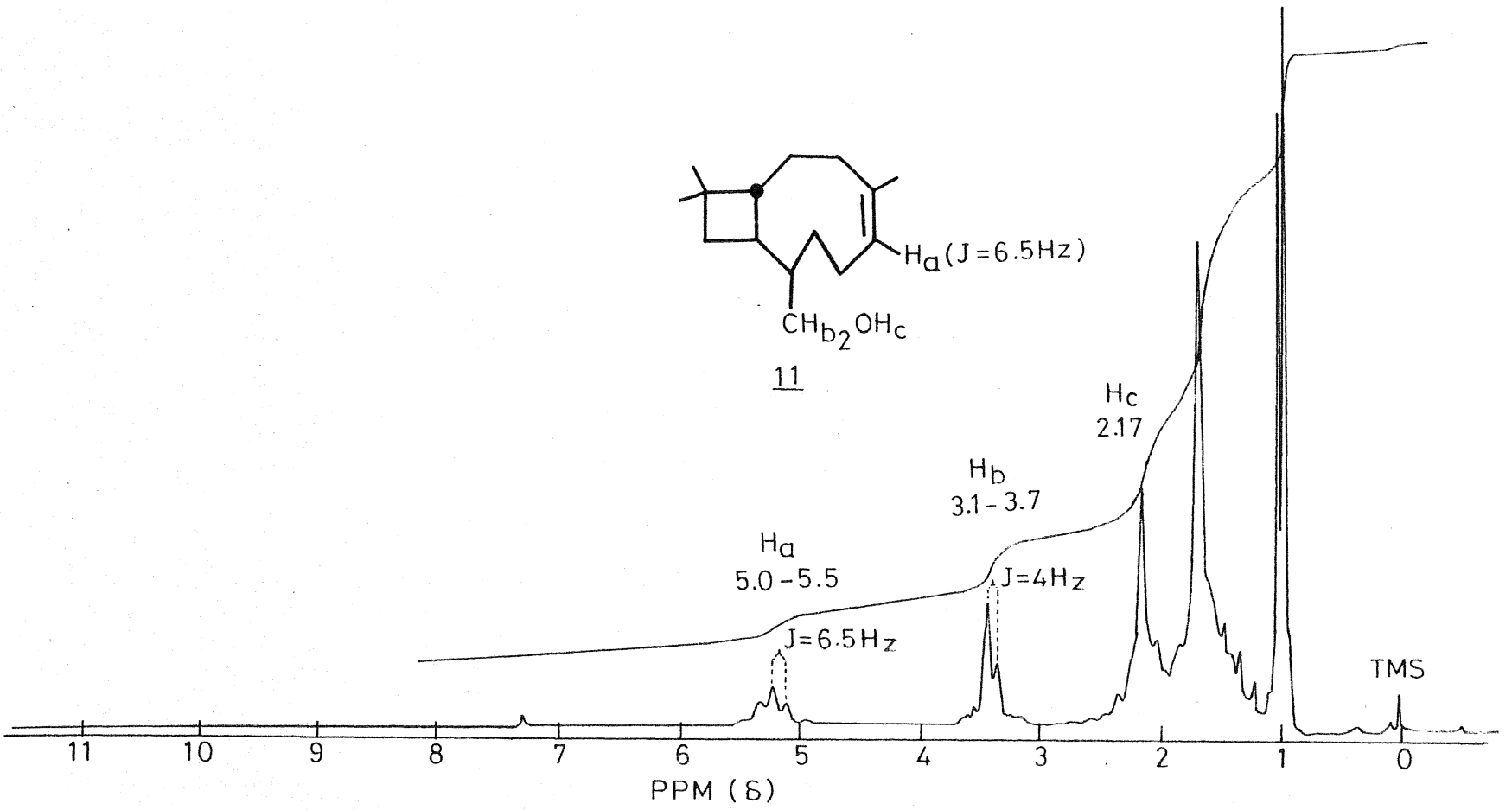


Fig. 1.12 NMR spectrum of isocaryophyllene alcohol (11).

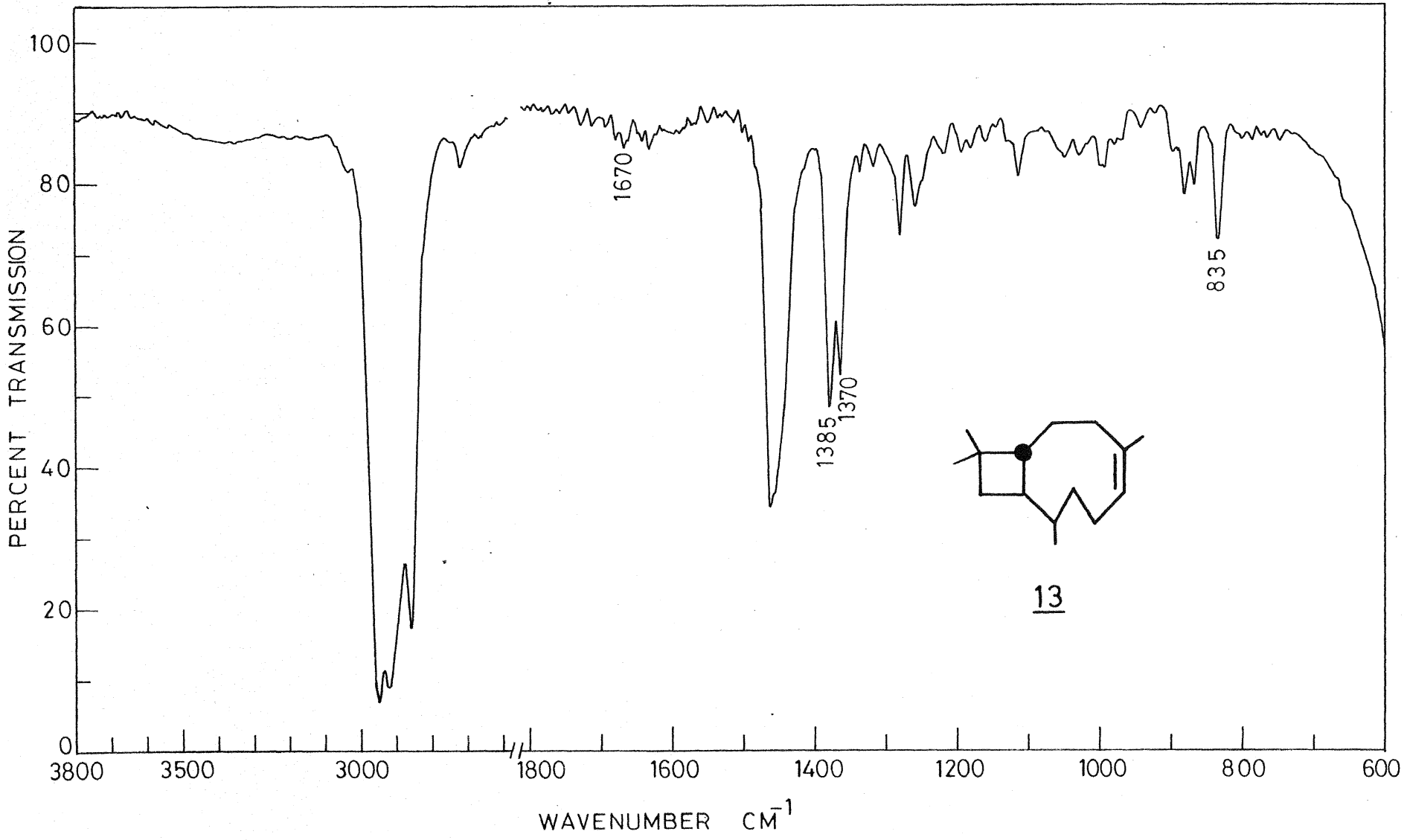


Fig. 1.13 IR spectrum of dihydroisocaryophyllene (13).

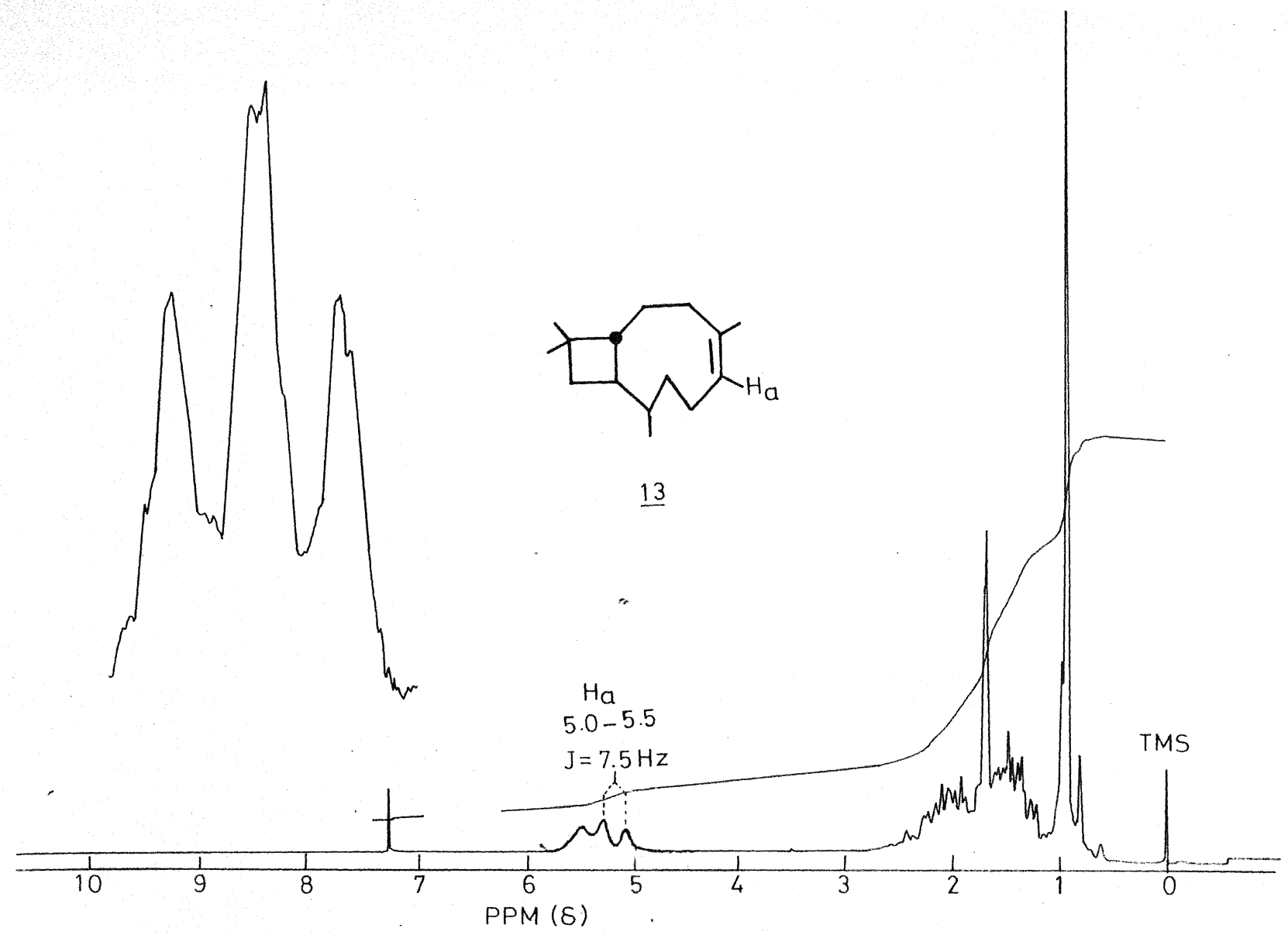


Fig.1.14 NMR spectrum of dihydroisocaryophyllene.(13).

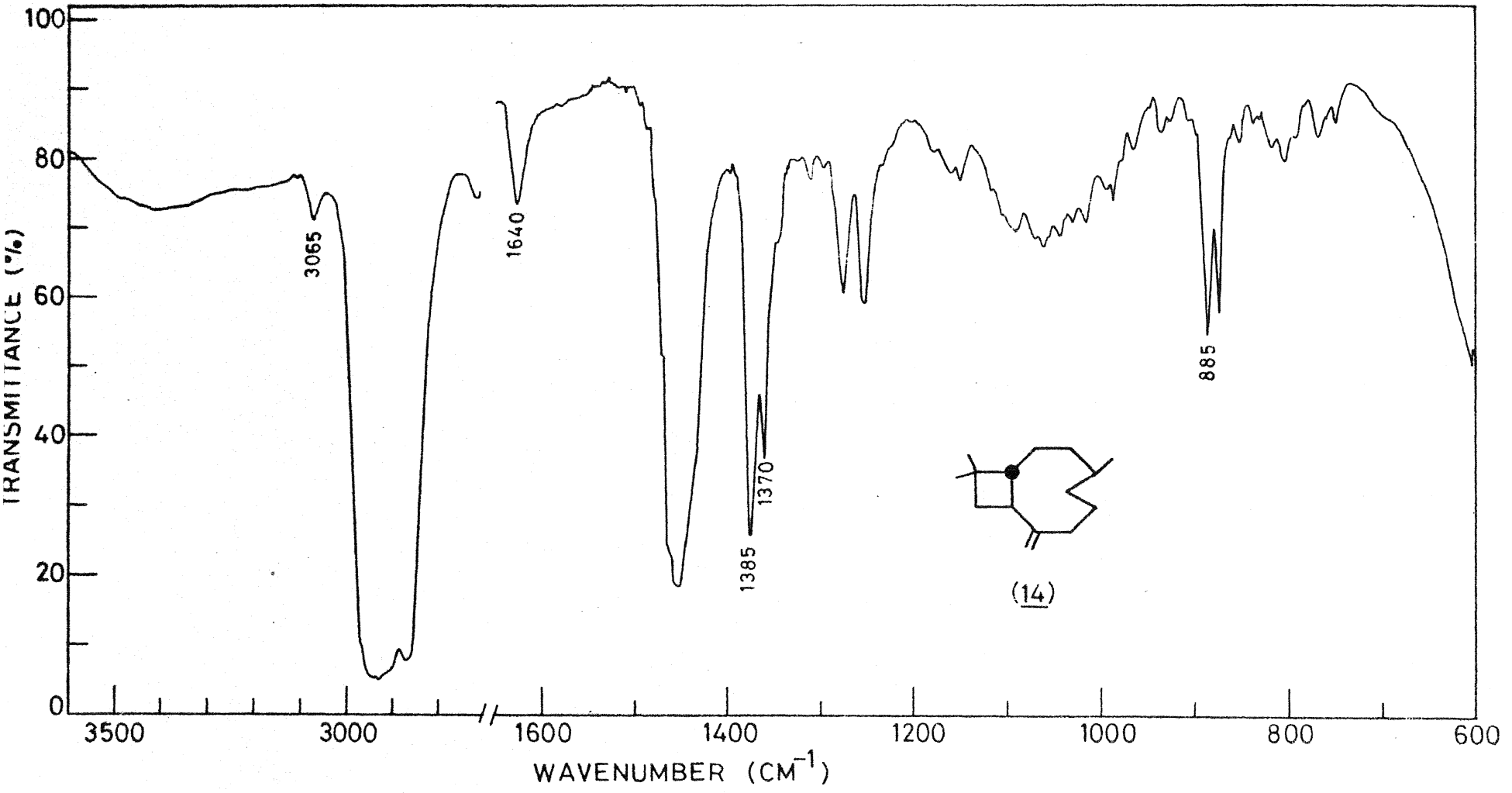


Fig. 1.15 IR spectrum of dihydrocaryophyllene (14).

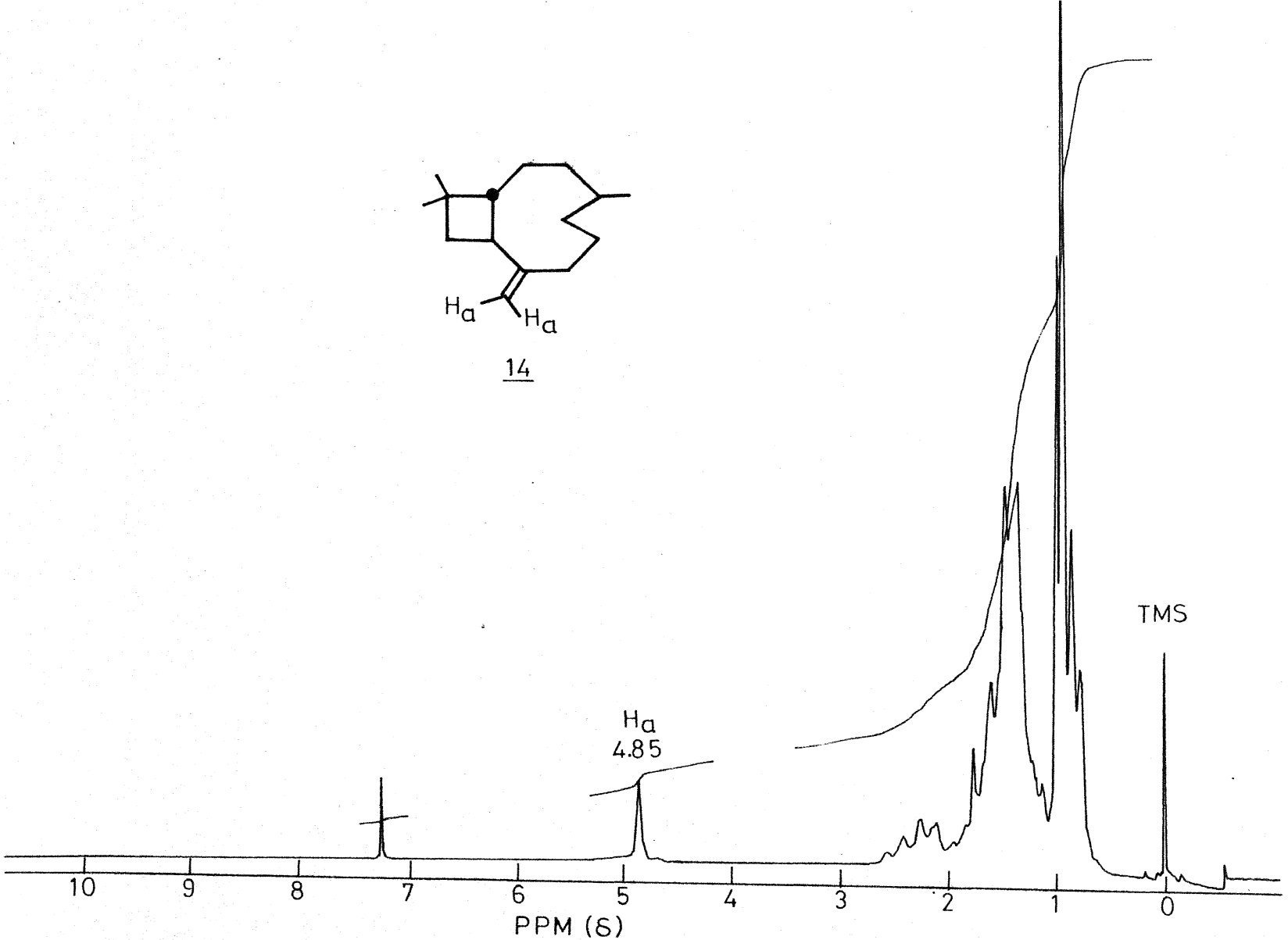


Fig.1.16 NMR spectrum of dihydrocaryophyllene (14).

Scientific Corporation, Avondale , Pa., U.S.A.). Microanalysis was done by Mr. A.H. Siddiqui of the Department of Chemistry, Indian Institute of Technology, Kanpur, India.

Materials

Caryophyllene obtained as a gift from late Prof. W. Parker was 85% pure by GLC analysis. Purification of the sample as described in literature[56] provided 98% pure sample, b.p. 84-85° (4 mm). Isocaryophyllene sample was generously donated by Prof. K.H. Schulte-Elte. Distillation of the sample at 83-84° (4 mm) provided >99% pure isocaryophyllene. Diglyme (Ansul Co.) was kept over calcium hydride for 24 hr, decanted and distilled over lithium aluminium hydride under reduced pressure, b.p. 63-64° (15 mm). Boron trifluoride etherate (BDH) was treated with small amount of dry ether and distilled under reduced pressure over calcium hydride, b.p. 46-47° (10 mm). Tetrahydrofuran (Pfizer) was kept over potassium hydroxide pellets overnight, decanted, refluxed over sodium wire for six hours, decanted and distilled over lithium aluminium hydride. Cyclohexene (Koch-light), silica-gel (Acme), pyridine (Pfizer), chromium trioxide (Sarabhai) and other chemicals used in the present investigation were used without further purification.

Preparation of Gas Liquid Chromatograph Columns

The liquid phase (weight depending upon the weight of solid support) was dissolved in minimum quantity of AR chloroform. The

solution of the liquid phase in chloroform was slowly added to the solid support (weight depending upon the length of the colum in a round-bottom flask with a standard joint. During the addition of solution constant shaking was done with the hand. After the addition was over thorough mixing of the liquid-phase with solid support was done with the help of a rotatory evaporator. The solvent was then removed under vacuum and finally dried in hot air oven. The column (1/4" dia.) was packed with solid support with constant tapping of the column so as to ensure uniform packing. Each column so packed was conditioned at different temperatures prior to use.

Purification of Caryophyllene[56]

Caryophyllene in light petroleum ether was washed several times with aqueous sodium hydroxide, then shaken with saturated aqueous silver nitrate. The organic extract was then dried, concentrated under reduced pressure and adsorbed on alumina. Elusion with light petroleum ether, removal of the solvent and distillation yielded pure caryophyllene, b.p. 84-85^{o} (4 mm). GLC analysis indicated it to be 98% pure.

Preparation of Borane in Tetrahydrofuran[12]

In a 500 ml three-necked flask fitted with a 250 ml pressure equalizing funnel, magnetic bar was connected through a tygon tubing to a dispersion tube, which was immersed in tetrahydrofuran (250 ml) contained in a 500 ml flask, which was cooled

externally with freezing mixture. The system was flushed with dry nitrogen. Then the three-necked flask was charged with sodium borohydride (19 g, 0.5 mol) in diglyme (125 ml). The pressure equalizing funnel was charged with boron trifluoride etherate (79 ml). Diborane wasgenerated by the dropwise addition of the boron trifluoride etherate over a period of 2-3 hours. After the addition was complete, the reaction flask was heated to 60° for 1 hour to drive the remaining diborane from diglyme into tetrahydrofuran solution. The sintered-glass tube was removed from tetrahydrofuran under a stream of nitrogen and transferred into a bottle. The resulting solution was 2 M in borane (BH_3) as standardized by measuring the hydrogen evolved on hydrolysis.

Hydroboration of Caryophyllene (2) with Dicyclohexylborane

A dry 100 ml flask equipped with a thermometer, a pressure equilibrated dropping funnel, a magnetic stirring bar and a mercury bubbler was assembled and flushed with dry nitrogen. In the flask was placed cyclohexene (3.28 g, 40 mmol) in tetrahydrofuran (20 ml) and was immersed in an ice-water bath. Dicyclohexylborane (20 mmol) was prepared by adding borane (10 ml, 2.0 M, 20 mmol) in tetrahydrofuran through the dropping funnel at 0° with magnetic stirring. The slurry thus obtained was stirred at 0-5° for 3 hours. To the dicyclohexylborane was added a solution of caryophyllene (2) (2.04 g, 10 mmol) in tetrahydrofuran (20 ml) with stirring at 0-5°. The reaction mixture was stirred for 2 hours at 0-5° and 2 hours at room temperature. The residual

hydride was destroyed with 1:10 mixture of water and tetrahydrofuran. Oxidation was carried out by adding sodium hydroxide (3 N, 3.2 ml) and hydrogen peroxide (30%, 3.2 ml). The reaction mixture was extracted with ether, the ether layer was washed with brine followed by ice-cold water. The ether layer was dried over anhydrous magnesium sulphate and distilled under vacuum to remove solvent and cyclohexanol. Column chromatography of the residue over basic alumina gave unreacted caryophyllene (2) (200 mg, 1 mmol) and caryophyllene alcohol (9) (1.4 g, 6.3 mmol) in 70% yield, b.p. 140-142°/(0.1 mm) based on recovered caryophyllene.

IR (CCl_4): 3625, 3400, 3080, 1640, 1385, 1370, 1070 and 885 cm^{-1}.

NMR ($CDCl_3$) δ ppm: 1.00 (3H, s), 1.03 (6H, s), 2.17 (1H, s), 3.5-3.7 (1H, m), and 4.87 (2H, s).

Anal. for $C_{15}H_{26}O$: Calcd C, 81.08; H, 11.71.
Found C, 80.72; H, 11.40%.

Pyridinium Chlorochromate Oxidation of Caryophyllene Alcohol (3)

A mixture of pyridinium chlorochromate (600 mg, 2.6 mmol) and fused sodium acetate (93 mg, 11 mmol) was suspended in dichloromethane (5 ml). Caryophyllene alcohol (9) (500 mg, 2.2 mmol) was rapidly added at room temperature with stirring. After two hours, the reaction mixture was diluted with anhydrous ether solvent (60 ml). The solvent was decanted and the black residue was washed with ether. The product mixture was isolated by filtration of the organic extracts through neutral alumina.

Evaporation of the solvent at reduced pressure and molecular distillation of the residue gave caryophyllene ketone (10) (360 mg, 1.6 mmol) in 72% yield, b.p. 120-122°/0.2 mm.

IR (CCl_4) : 3060, 1715, 1640, 1385, 1370 and 885 cm^{-1}.

NMR ($CDCl_3$), δ ppm: 4.95 and 4.85 (2H, s) and 0.90-2.50 (22H, m).

Anal. for $C_{15}H_{24}O$: Calcd C, 81.83; H, 10.91.
Found C, 81.48; H, 10.73%.

Hydroboration of Isocaryophyllene (3) with Dicyclohexylborane

Monohydroboration of isocaryophyllene (3) (2.04 g, 10 mmol) with dicyclohexylborane (20 mmol) was carried out in a manner similar as described above to obtain unreacted isocaryophyllene (3) (200 mg, 1 mmol) and isocaryophyllene alcohols (11 + 12) (1.3 g, 5.9 mmol) in 65% yield based on the recovered isocaryophyllene, b.p. 142-143°/0.1 mm.

IR (CCl_4) : 3650, 3400, 1640, 1385, 1370, 1030, 890 and 835 cm^{-1}.

NMR ($CDCl_3$), δ ppm: 0.94 (s), 0.97 (s), 1.6 (d, J = 2.0 Hz), 5.0-5.5 (t, J = 6.5 Hz) and 4.7-5.0 (m).

Anal. for $C_{15}H_{26}O$: Calcd C, 81.08; H, 11.71.
Found C, 80.72; H, 11.30%.

Hydroboration of Caryophyllene (2) with Thexylborane

In a 100 ml three-necked flask, fitted with a magnetic stirring bar, a thermometer and a mercury bubbler was placed

borane (1 M, 50 ml, 50 mmol) in tetrahydrofuran. To this was added at 0° 2,3-dimethyl-2-butene (4.2 g, 50 mmol). The reaction mixture was stirred for 1 hour at 0° and used as a stock solution of thexylborane in tetrahydrofuran. It was found to be 0.5 molar solution upon hydrolysis of a known volume of the reagent.

Thexylborane (0.5 M, 20 ml, 10 mmol) in tetrahydrofuran and caryophyllene (2) (2.04 g, 10 mmol) in tetrahydrofuran (20 ml) were added dropwise simultaneously into a flask containing tetrahydrofuran (20 ml) at 0° with stirring, over a period of thirty minutes. The reaction mixture was stirred for 1 hour and then stirred at room temperature for an additional 2 hours. The usual oxidation of the organoborane using sodium hydroxide (6 N, 3.2 ml) and hydrogen peroxide (30%, 3.2 ml) followed by work-up procedure as already described, provided unreacted caryophyllene (2) (1.2 g, 5.9 mmol) and caryophyllene alcohol (9) (0.7 g, 3.1 mmol) in 76% yield. The IR, NMR and GLC retention times were identical with the sample obtained earlier.

Hydroboration of Isocaryophyllene (3) with Thexylborane

Hydroboration of isocaryophyllene (3) (2.03 g, 10 mmol) using thexylborane (0.5 M, 20 ml, 10 mmol) as described above followed by oxidation yielded unreacted isocaryophyllene (3) (1.15 g, 5.6 mmol) and isocaryophyllene alcohol (11) (0.65 g, 2.9 mmol) in 67% yield, b.p. 141-142°/0.1 mm.

IR (CCl_4): 3650, 3400, 1670, 1385, 1370, 1040 and 840 cm^{-1}.

NMR ($CDCl_3$), δ ppm: 0.94 (3H, s), 1.00 (3H, s), 1.70 (3H, s), 2.17 (1H, s), 3.1-3.7 (2H, d, J = 4.0 Hz) and 5.0-5.5 (1H, t, J = 6.5 Hz).

Anal. for $C_{15}H_{26}O$: Calcd C, 81.08; H, 11.71.
Found C, 80.83; H, 11.43%.

Hydroboration-Protonolysis of Isocaryophyllene (3)

Hydroboration of isocaryophyllene (3) (4.08 g, 20 mmol) in tetrahydrofuran (40 ml) with dicyclohexylborane (40 mmol), prepared from cyclohexene (6.56 g, 80 mmol) in tetrahydrofuran (40 ml) and borane (2.0 M, 20 ml, 40 mmol) in tetrahydrofuran, was carried out as described previously. The unreacted isocaryophyllene (3) (0.42 g, 2 mmol) and tetrahydrofuran were removed from the organoboranes under vacuum. The organoboranes were treated with propionic acid (5 ml) and refluxed for 8 hours. The reaction mixture was cooled and sufficient amount of sodium hydroxide (3N) was added to ensure an excess. The reaction mixture was then extracted with cyclohexane, washed several times with water till neutral and dried over anhydrous magnesium sulphate. Purification by filtering through a short column of silica gel, removal of the solvent followed by distillation gave dihydroisocaryophyllene (13) (2.1 g, 10.2 mmol) in 57% yield, b.p. 110°/12 mm.

IR (neat): 1670, 1385, 1370 and 835 cm^{-1}.

NMR ($CDCl_3$), δ ppm: 0.94 (3H, s), 1.00 (3H, s), 1.66 (3H, d, J = 1.2 Hz) and 5.0-5.5 (1H, t, J = 7.5 Hz).

Anal. for $C_{15}H_{26}$: Calcd C, 87.38; H, 12.62.
Found C, 87.10; H, 12.58%.

Partial Diimide Reduction of Caryophyllene (2)

In a 250 ml three-necked flask fitted with a gas outlet, a magnetic stirrer and a pressure-equilibrated dropping funnel, was placed a solution of caryophyllene (2) (2.04 g, 10 mmol) in 95% ethanol (60 ml). To this solution 98% hydrazine hydrate (2 g, 40 mmol) and copper sulphate solution (1%, 1 ml) were added. The contents were stirred and cooled by ice-salt mixture. The gas outlet was led into a water filled measuring cylinder to measure the volume of nitrogen evolved. After the system was steady, hydrogen peroxide (30%, 6 ml) was added through the dropping funnel at the rate of 5-6 drops per minute. After the complete evolution of nitrogen, water was added to the reaction mixture. Then product was extracted three to four times with n-hexane and the combined extracts, after washing with water, was dried over anhydrous magnesium sulphate. Evaporation of the solvent followed by distillation provided dihydrocaryophyllene (14) (1.8 g, 8.7 mmol) in 87% yield, b.p. 110-112°/12 mm. GLC analysis on a 15' Carbowax 20 M column indicated it to be 98% pure.

IR (neat): 3065, 1640, 1385, 1370 and 885 cm^{-1}.

NMR ($CDCl_3$), δ ppm: 0.95 (6H, s), 1.00 (3H, s) and 4.85 (2H, s).

Anal. for $C_{15}H_{26}$: Calcd C, 87.38; H, 12.62.
Found C, 87.10; H, 12.56%.

Partial Diimide Reduction of Isocaryophyllene (3)

Partial diimide reduction of isocaryophyllene (2.04 g, 10 mmol) as described above indicated 80% conversion to dihydroisocaryophyllene (13) (98% GLC yield) as analysed by GLC. Pure dihydroisocaryophyllene was obtained by preparative GLC. The IR, NMR and GLC retention times were identical with the sample obtained by isocaryophyllene, hydroboration-protonolysis experiment.

Anal. for $C_{15}H_{26}$: Calcd C, 87.38; H, 12.62.
Found C, 87.10; H, 12.56%.

I.5 REFERENCES

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CHAPTER II

DIHYDROBORATION CHROMIUM TRIOXIDE OXIDATION OF *gem*- AND *vic*-DIORGANOBORANES[1]

II.1 ABSTRACT

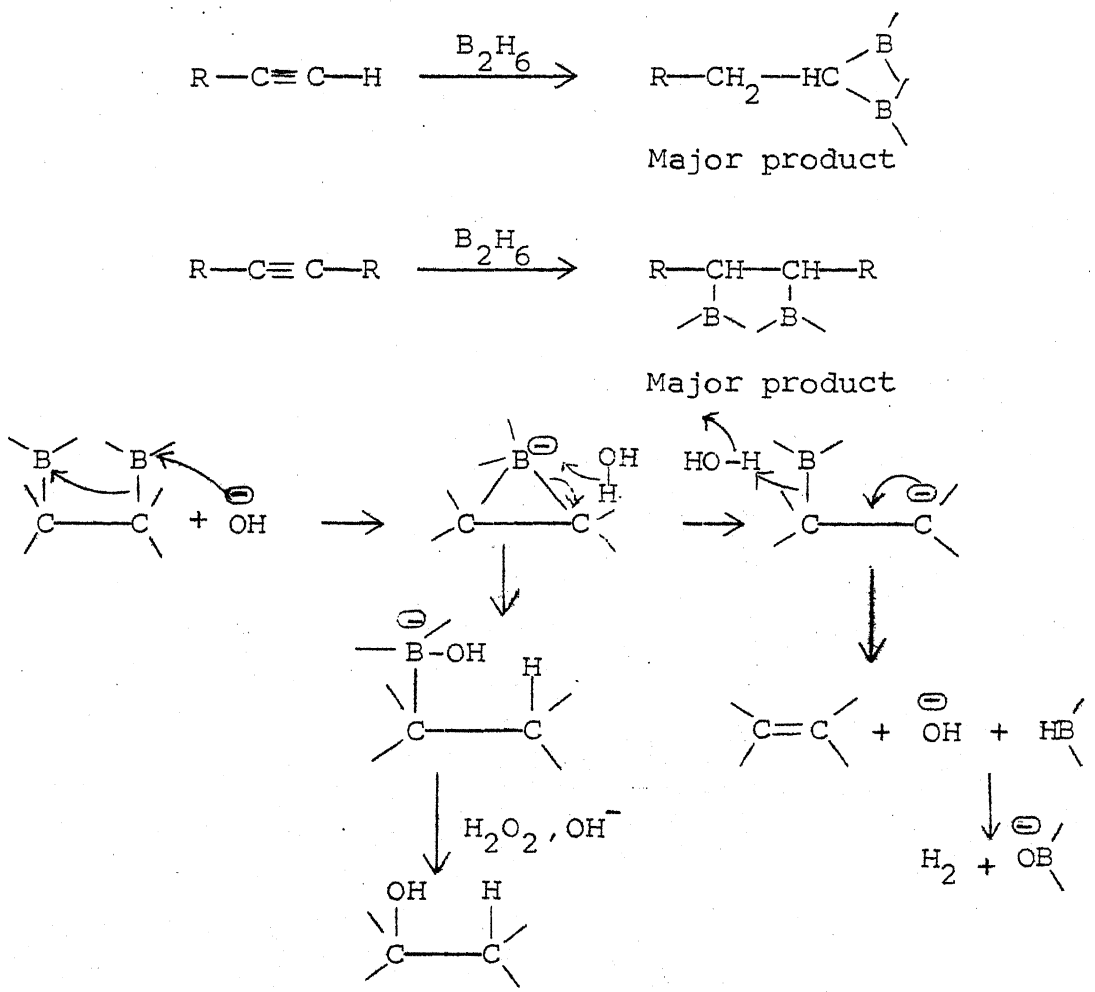
Representative cyclic and acyclic acetylenes were dihydroborated using BH_3-THF, and the resulting mixture of 1,1- and 1,2-diorganoboranes was treated with chromium trioxide in pyridine. It appears that the 1,1-diorganoboranes are transformed to the corresponding alcohols and ketones, while the *threo*-1,2-diorganoboranes mainly give (*E*)-olefins *via* a *cis* stereospecific elimination.

II.2 INTRODUCTION

The *gem*- and *vic*-diorganoboranes have been obtained from the dihydroboration of acetylenes. The dihydroboration of acetylenes followed by alkaline hydrogen peroxide oxidation has been extensively studied by several group of workers.[2-5] Dihydroboration of terminal acetylenes is known to give *gem*-diorganoborane as the major product, while internal acetylenes

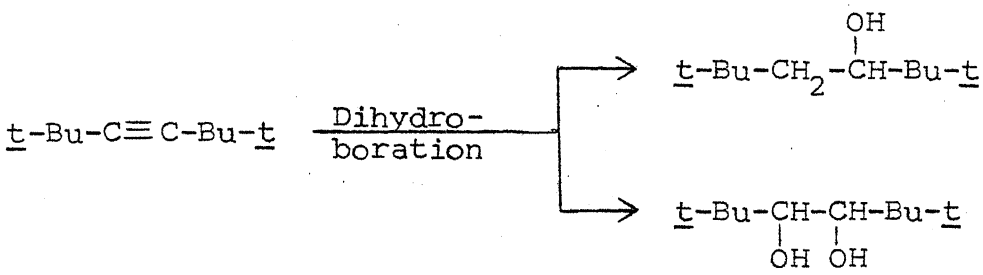
give mainly vic-diorganoborane. The alkaline hydrolysis of gem- and vic-diorganoboranes has been extensively studied by Pasto.[4] Based on deuterium incorporation, it has been suggested that the vic-diorganoborane undergoes an exceedingly rapid, base-catalyzed hydrolysis. The possibility of neighbouring boron participation during the hydrolysis of vic-diorganoborane has been explored. The proposed bridged boron anion is capable of undergoing hydrolysis to give monoorganoborane, which on oxidation gives alcohol. It can also undergo elimination to give olefin (Scheme II.1):

Scheme II.1



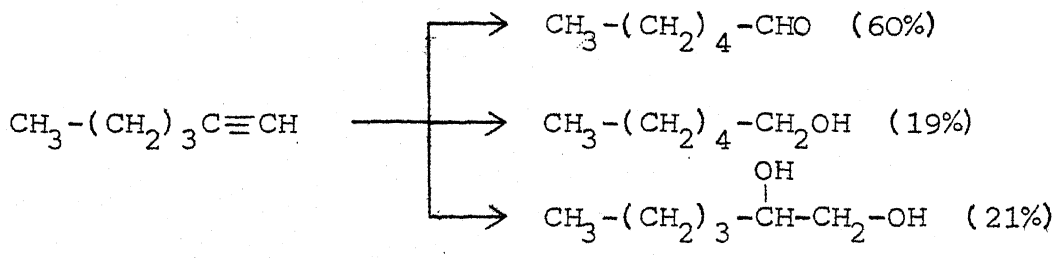
Logan and Flautt[2] isolated 2,2,5,5-tetramethyl-3-hexanol and 2,2,5,5-tetramethyl-3,4-hexane diol from dihydroboration of di-t-butyl acetylene (Scheme II.2). These authors rationalized the formation of alcohol as possibly occurring by reduction of the corresponding carbonyl compound, formed by hydrolysis and oxidation, by some reducing species ($\backslash B\text{-}H$) present in the mixture.

Scheme II.2



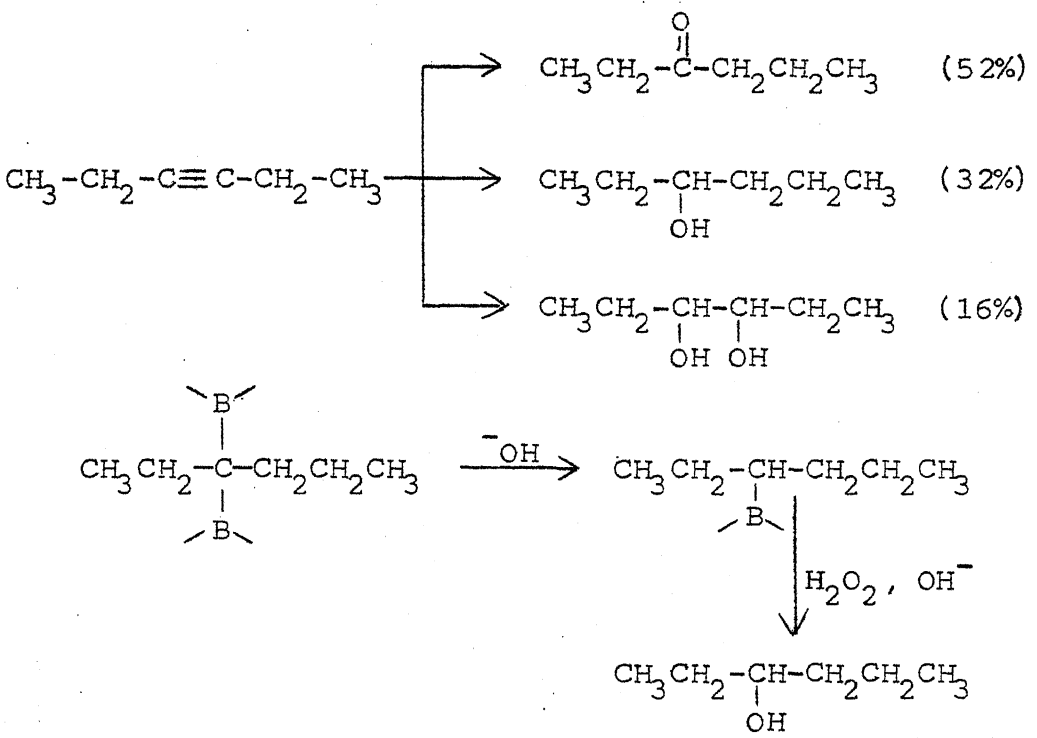
Brown and Zweifel[6] isolated 1-hexanal, 1-hexanol and 1,2-hexane diol from dihydroboration of 1-hexyne and 3-hexanone, 3-hexanol and 3,4-hexane diol from 3-hexyne. From evidences gathered from the dihydroboration of 1-hexyne, the authors visualized the formation of 3-hexanol as occurring via a base catalyzed hydrolysis of gem-diorganoborane to monoorganoborane followed by oxidation (Scheme II.3):

Scheme II.3



.....contd

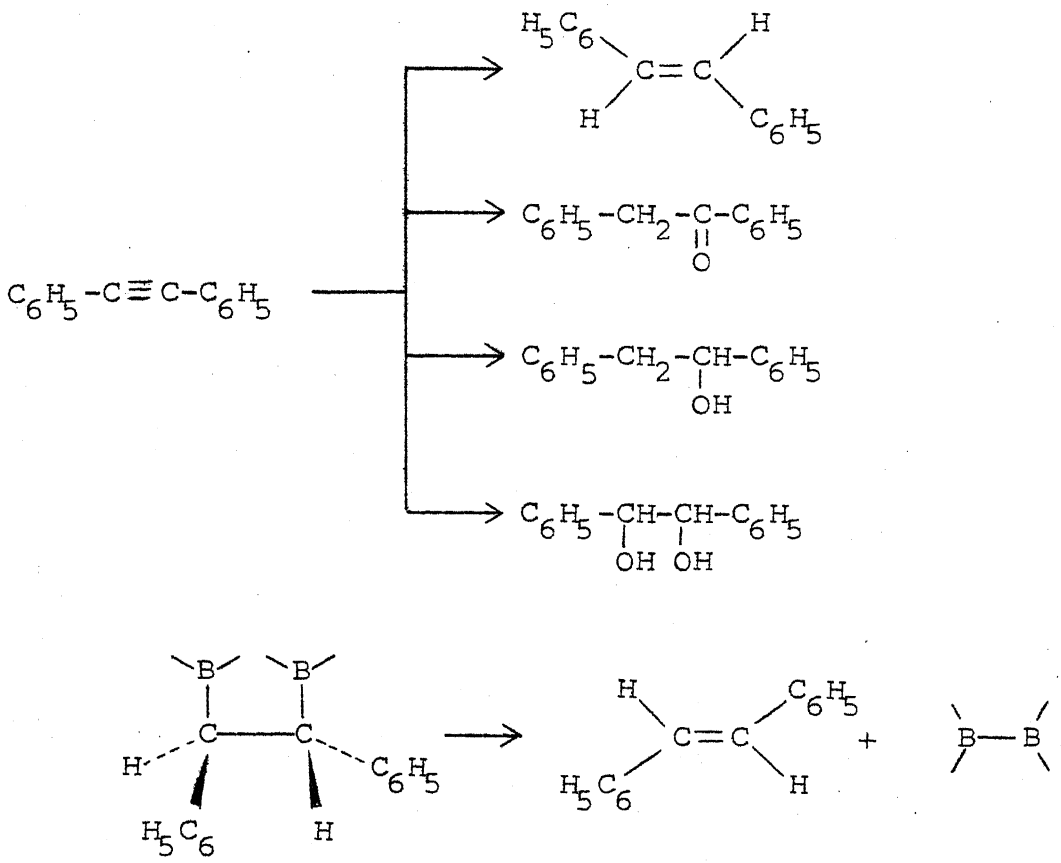
Scheme II.3 (contd.)



Hassner and Braun[3] isolated (E)-stilbene, deoxybenzoin, 1,2-diphenylethanol and dl-hydrobenzoin from dihydroboration of diphenylacetylene. The formation of (E)-stilbene was postulated as arising by the elimination of boron-boron bonded species from vic-diorganoborane as shown in Scheme II.4.

However, the proposed mechanism by Hassner and Braun[3] was in direct contradiction with the mechanism of Pasto and Miesel[7,8] for such an elimination. According to Pasto and Miesel the β-substituent to the boron atom must possess a non-bonded electron pair capable of complexing with boron to initiate the reaction relieving the instability and the stereochemistry must be such as

Scheme II.4

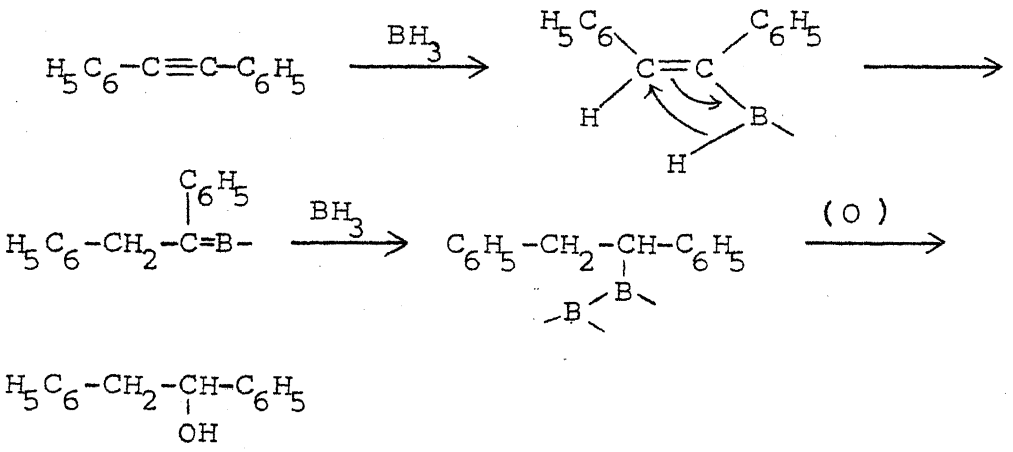


to allow intramolecular complexation to occur. In this case the β-boron has no non-bonded pair of electrons and therefore, the vicinal diborocompound is expected to be stable towards such an elimination reaction. In addition, the reverse of this postulated elimination is known to occur.[9-11]

Hassner and Braun[3] also suggested a possible mechanism for the formation of monoalcohol. This may occur <u>via</u> hydroboration of a postulated intermediate formed by an intramolecular hydride shift in vinyl organoborane, followed by oxidation

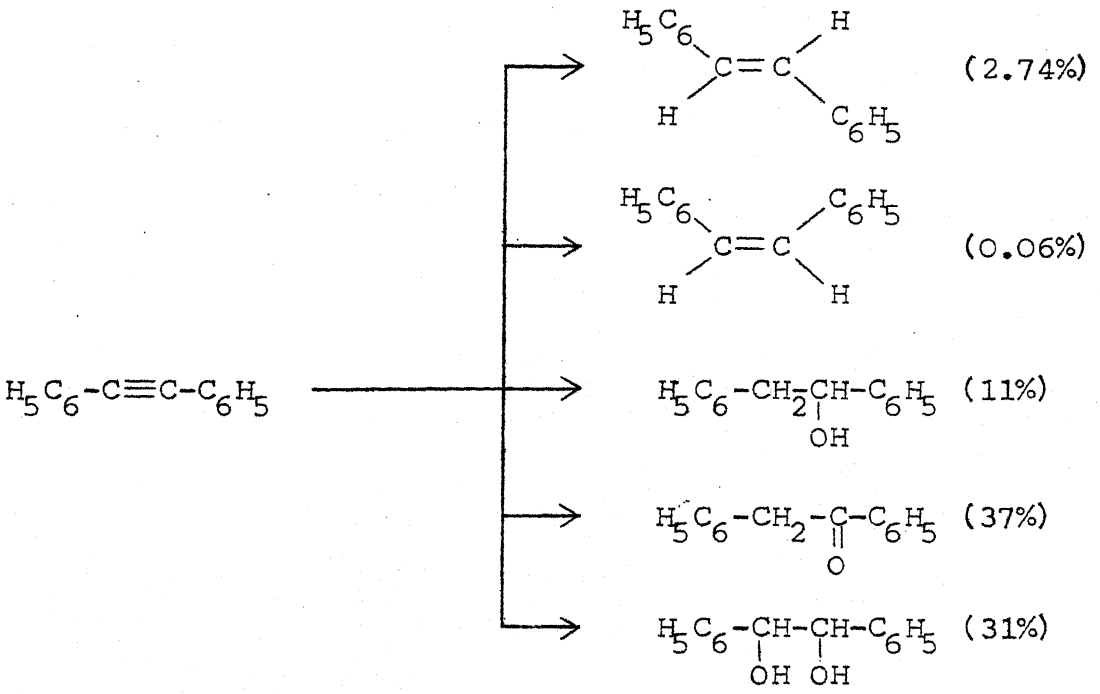
(Scheme II.5):

Scheme II.5



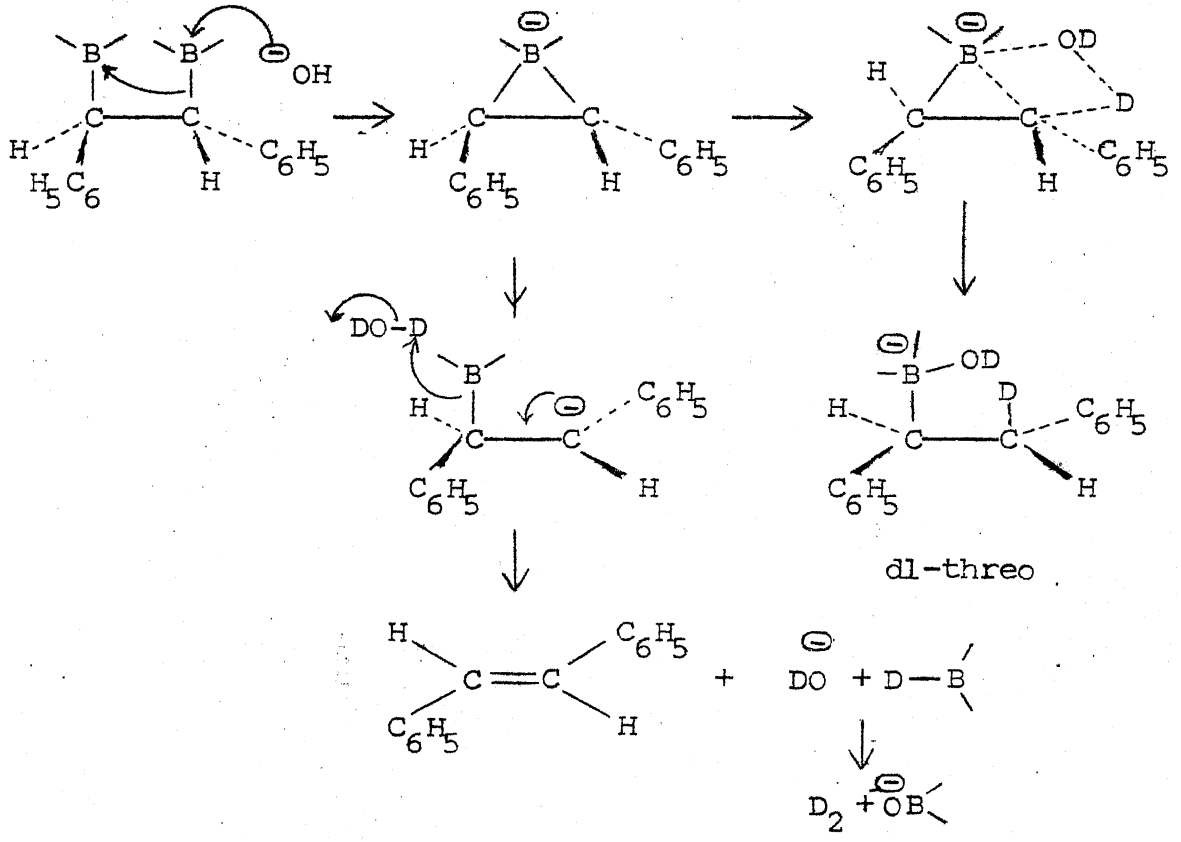
At this stage Pasto[4] did a detailed study on the dihydroboration of diphenylacetylene and isolated small amount of cis-stilbene and dibenzyl along with a mixture of products as reported by Hassner and Braun[3] (Scheme II.6):

Scheme II.6



The deuterium labelling studies have indicated that many of the previously suggested mechanisms are not operative and that the vic-diorganoborane is the precursor for olefin, monoalcohol and 1,2-diol, in the case of internal acetylenes. The labelling experiments have indicated that the vic-diorganoborane undergoes exceedingly rapid base catalyzed hydrolysis indicating participation by neighbouring boron during hydrolysis. The proposed bridged anion may undergo elimination to give (E)-stilbene, deuterolysis to give monoorganoborane which on oxidation gives β-deuterioalcohol (Scheme II.7):

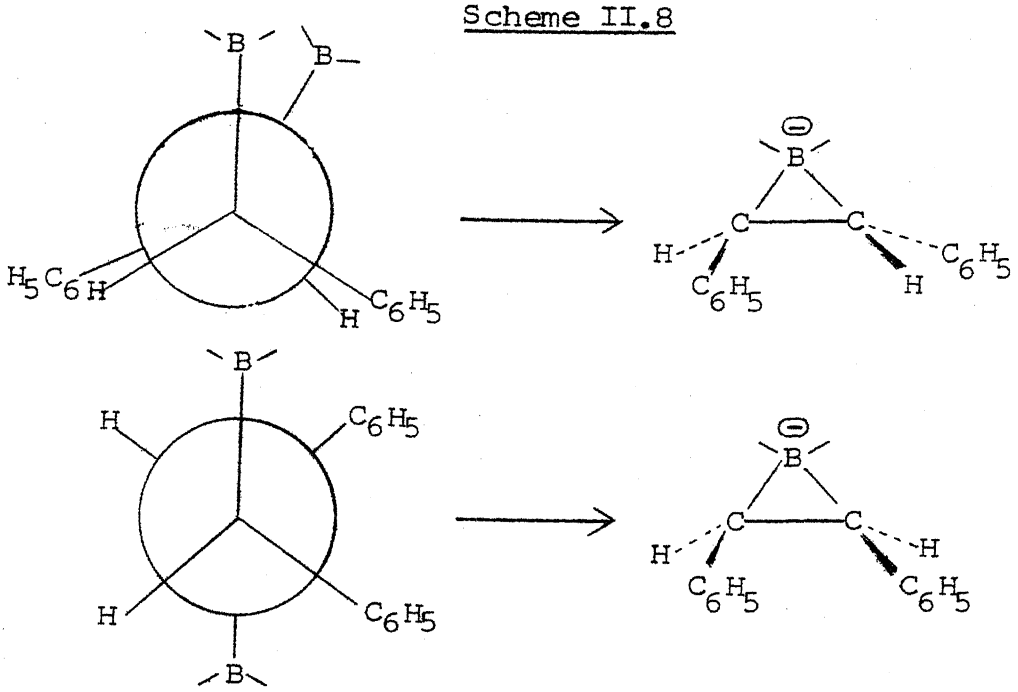
Scheme II.7



The inability to detect olefin prior to deuterolysis and detection of cis-stilbene were not compatible with an elimination of a boron-boron bonded species. The stereochemistry of the intermediate vic-diorganoborane formed by two cis-additions of $\diagdown$B-H to carbon-carbon triple bond would require the formation of (E) stilbene from diphenylacetylene. The possibility for the formation of olefin by the hydrolysis of a vinylic carbon-boron bond has been eliminated by the lack of deuterium incorporation in the olefin during deuterolysis.

The monoalcohol was shown not to be formed exclusively by hydrolysis of the gem-diorganoborane followed by oxidation as suggested by Brown and Zweifel[6] or by hydroboration of the intermediate organoborane having a carbon-boron double bond or by reduction of an intermediate carbonyl compound during work-up as evidenced by the incorporation of deuterium at positions 1 and 2 of 1,2-diphenylacetylene. The rate of deuterium incorporation at 1 and 2 positions were comparable and considerably faster than deuterolysis of monoorganoborane. The enhanced rate of deuterolysis of carbon-boron bond of the vic-diorganoborane has been explained by involving the participation of the neighbouring boron in two ways during carboanion formation as (E)-stilbene is formed in great excess over the (Z)-stilbene. It would appear that the anion with retention of configuration is preferred over the anion with inversion (Scheme II.8):

Scheme II.8



The 1D-1,2-diphenyl ethanol was evidently obtained from a gem-diorganoborane through deuterolysis followed by oxdiation (Scheme II.9). The deoxybenzoin is formed directly from the gem-diorganoborane. The results of Pasto are summarised in Table II.1.

Scheme II.9

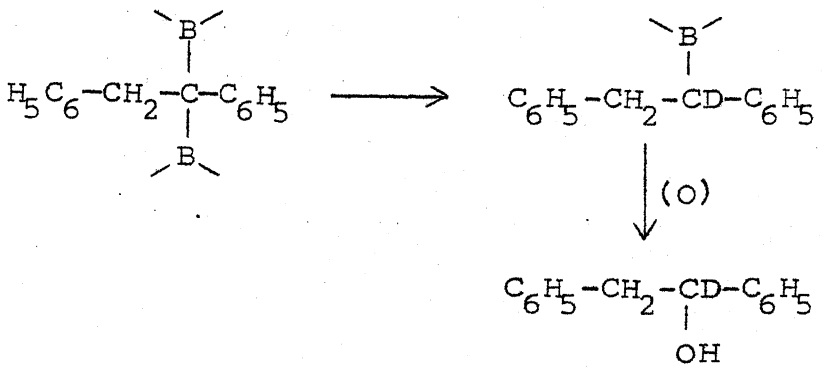


Table II.1

Composition of the Dihydroboration Product from Acetylenes

Acetylene	Product		
	Vicinal	Geminal	Mono
Diphenylacetylene	67	18	15
Phenylacetylene	42	38 (terminal)	17
		3 (internal)	
1-Hexyne	30	62	8
3-Hexyne	36	32	32

But the results of Pasto[4] were contradicting the results of Brown[6] in the amounts of vic- and gem-diorganoboranes formed from the dihydroboration of 1-hexyne. In view of the increasing interest in these difunctional boro compounds as useful intermediates in synthetic work Zweifel did a detailed study to resolve the descrepancy.

1-Hexyne (25 mmol) was hydroborated at 0° with a solution of borane in tetrahydrofuran (18.3 mmol of BH_3). The resulting deep yellow solution was maintained for 1 hour at 0° before diluting with sodium hydroxide (3N, 7.5 ml). Measurement of the hydrogen evolved revealed that the hydroboration did not proceed to completion, but utilized 1.92 to 1.95 "hydrides" per acetylene molecule. After being kept at 0-25° for varying

lengths of time, the reaction mixture was oxidized with alkaline hydrogen peroxide and the products formed were examined by GLC. It should be noted that the vinylborane, which originates from incomplete hydroboration, is the source of 5-8% of the hexaldehyde obtained. The experimental results are summarized in Table II.2.

Table II.2

Hydrolysis of the Dihydroborated 1-Hexyne with Sodium Hydroxide Followed by Oxidation with Alkaline Hydrogen Peroxide

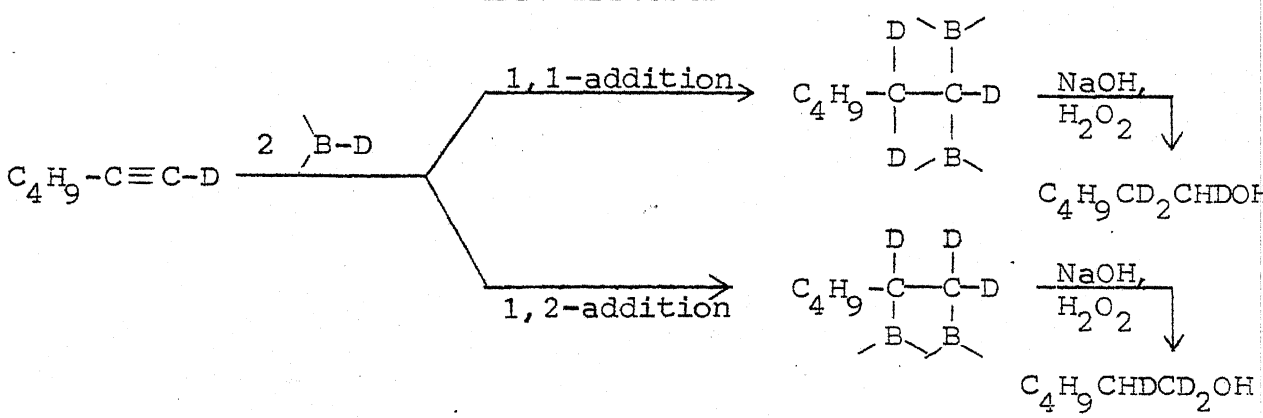
Hydrolysing time (hr)	Temp. (°C)	1-Hexanol	Hexaldehyde	1,2-Hexane diol	2-Hexanol, 2-Hexanone
0	0.5	55	28	10	7
2	0.5	62	22	11	5
8	0.5	69	16	11	4
1	25.0	71	14	10	5
2	25.0	74	11	10	5
4	25.0	80	5	10	5

It is evident that part of the dihydroboration product must undergo an exceedingly fast hydrolysis to n-hexylborane, which is then oxidized to 1-hexanol. The fact that the yield of 1-hexanol increases at the expense of the aldehyde during the slow hydrolysis step (Table II.2) indicated that this portion of the alcohol is formed from the gem-diorganoborane.

It is noteworthy that 10-12% of glycol, which must arise from the 1,2-diorganoborane, remains essentially constant under the various reaction times. This could mean either that hydroboration gives only a small amount of the vic-diorganoborane, which is resistant to hydrolysis, or that the partially hydrolyzed 1,2-diorganoborane with hydroxy groups attached to the boron resists further cleavage. The latter view is supported by the fact that ethane 1,2-diboronic acid is stable to hydrolysis.[10]

Hydroboration of 1-hexyne with deuteriodiborane offers a convenient method for distinguishing between 1,1- and 1,2-addition. Hydroboration of 1-hexyne-1-d with deuteriodiborane (98% D) was carried out as described above and the dihydroboration product formed was treated with sodium hydroxide (3 N). The mixture was kept for 2 hours at room temperature, then was oxidized in the usual way. The 1-hexanol formed was isolated by preparative GLC and was examined by nuclear magnetic resonance. Using the hydroxyl proton as an internal standard, the spectrum revealed the presence of 1.00 ($\pm$0.03) deuterium in position 1 and 1.97 ($\pm$0.02) deuteriums in position 2 (Scheme II.10):

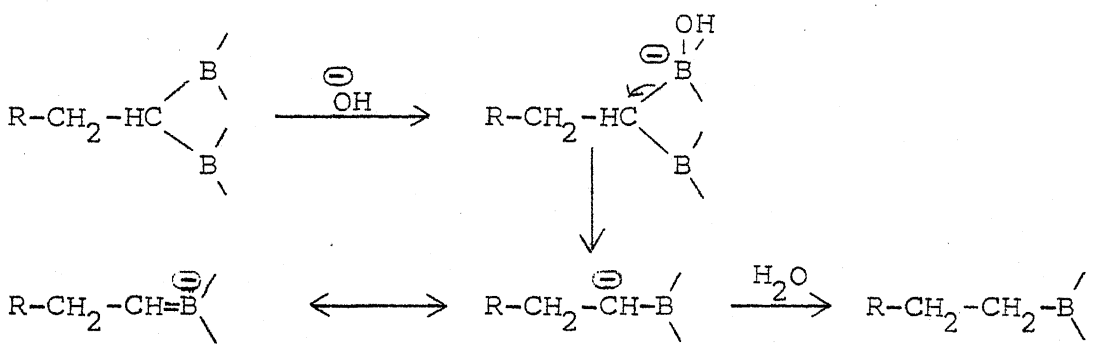
Scheme II.10



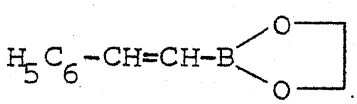
The results clearly demonstrate that the dihydroboration of 1-hexyne with diborane proceeds to place atleast 80% of the boron atoms at the terminal carbon atom and that no detectable amount of 1-hexanol arises from the hydrolysis of a 1,2-diorganoborane. Finally the dihydroboration product when treated with m-chloroperbenzoic acid (3 mol) showed hexanoic acid in 79% yield. It is evident that only the geminal dihydroboration intermediate yields a carboxylic acid on oxidation.

The hydrolytic instability of the gem-diorganoborane can be rationalized in terms of a nucleophilic attack by base on boron with the resulting intermediate carbanion being stabilized by interaction with the vacant p orbital of the adjacent boron atom[5] (Scheme II.11):

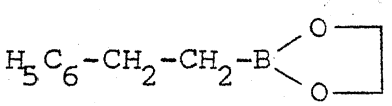
Scheme II.11



In order to clarify the mode of formation of the unexpected oxidation products[4] Pasto synthesized the model compounds[12] (1-6):



1



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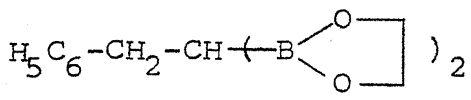
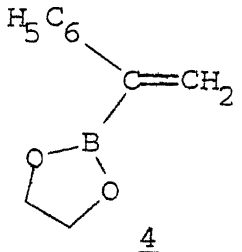


3



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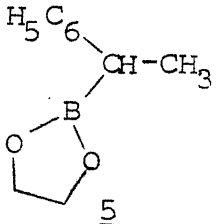

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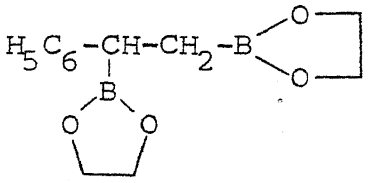
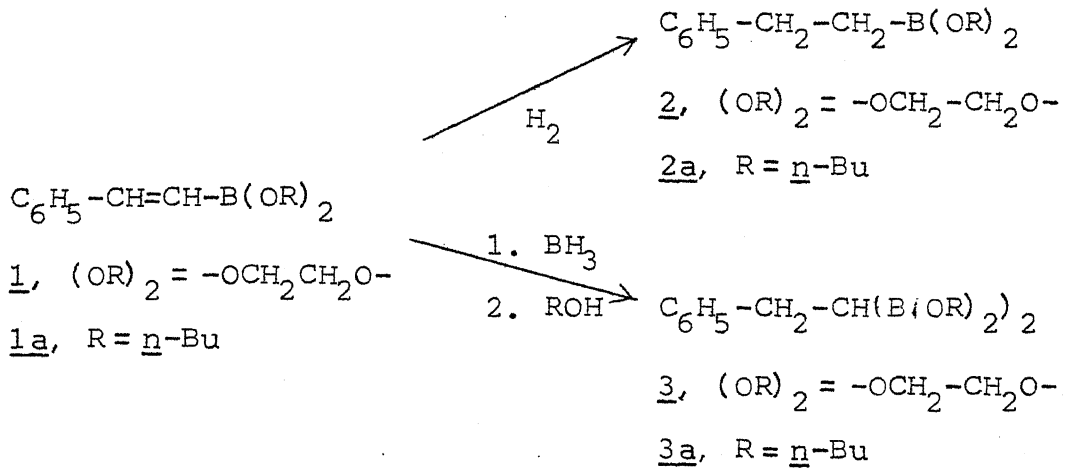


6

Dibutyl β-styreneboronate(1a), was prepared as a mixture of the cis and trans-isomers by reaction of β-styrylmagnesium-bromide with trimethylborate at -70°. Dibutyl 2-phenylethane-borate (2a) was prepared by catalytic hydrogenation of 1a in n-butanol. The ethylene esters of 1 and 2 were prepared by treatment of 1a and 2a with ethylene glycol followed by distillation. Hydroboration of 1a with an excess of borane in tetrahydrofuran, followed by the addition of n-butanol and direct distillation, provided tetrabutyl 2-phenylethane-1,1-bisboranate (3a). 3a was converted to the diethylene ester 3 by treatment with ethylene glycol (Scheme II.12). Compounds 4, 5 and 6 were prepared in a similar manner from dibutyl α-styreneboronate.

Pasto[13] oxidized compounds 1, 2, 4 and 5 with basic hydrogen peroxide, to get the expected alcohols and carbonyl compounds. Similar treatment of 3 gave a number of products, of which the C-C bond cleavage products, benzaldehyde and

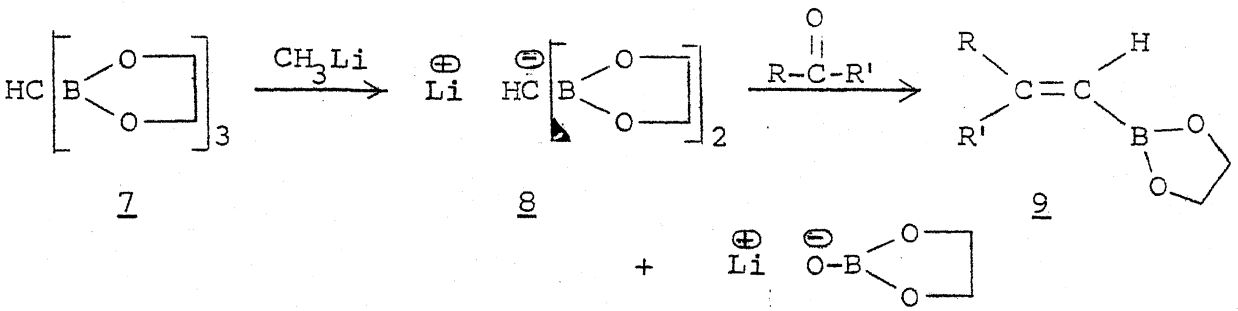
Scheme II.12



benzylalcohol predominate (upto 60% and 20% respectively). Basic hydrogen peroxide oxidation of 6 similarly produced a number of products including benzaldehyde and acetophenone.[13] The formation of the abnormal products has been visualised by radical reactions involving hydroxyl or hydroperoxyl radicals which can form in basic solutions of hydrogen peroxide.

Recently Matteson[14-16] reported convenient procedures for preparing 1,1-diboronic esters as illustrated in Scheme II.13:

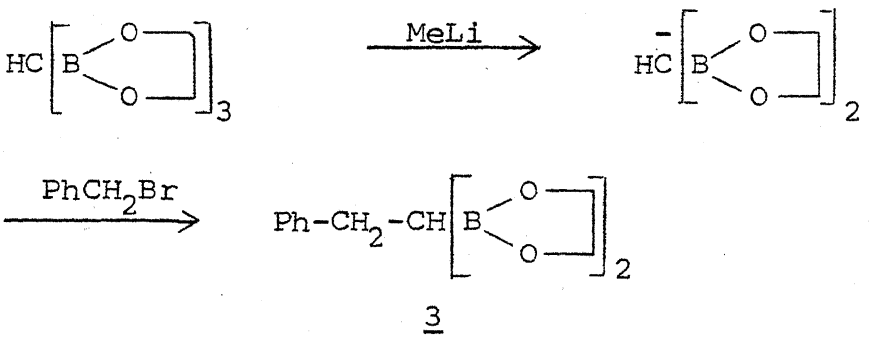
Scheme II.13



Tris(ethylenedioxyboryl)methane (7) with methyllithium yields lithium bis(ethylenedioxyboryl)methide (8), which reacts with aldehydes or ketones to give high yields of alkeneboronic esters (9).

Tris(ethylenedioxyboryl)methane was converted to the carbanion with methyllithium which reacted with benzylbromide to form 1,1-bis(ethylenedioxyboryl)-2-phenylethane[17] (3) (Scheme II.14):

Scheme II.14

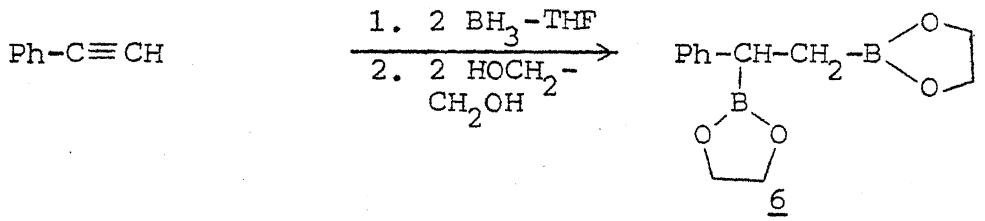


3

Matteson latter attempted a shorter route to 1,1-bis-(ethylenedioxyboryl)-2-phenylethane by direct hydroboration of phenylacetylene. The literature indicates that hydroboration of vinylboranes or dihydroboration of terminal acetylenes preferentially places both boron atoms on the terminal carbon.[12,18,5] An early paper by Pasto suggesting substantial formation of 1,2-diboryl compound in the dihydroboration of phenylacetylene[4] was latter questioned by Zweifel and Arzoumanian[5] and agreed to be inconclusive by Pasto and coworkers.[13] It therefore was a

considerable surprise to obtain a 55% yield of crystalline 1,2-bis(ethylenedioxyboryl)-1-phenylethane (6), the "wrong" isomer, from the dihydroboration of phenylacetylene with two moles of borane in tetrahydrofuran followed by treatment with ethylene glycol (Scheme II.15):

Scheme II.15

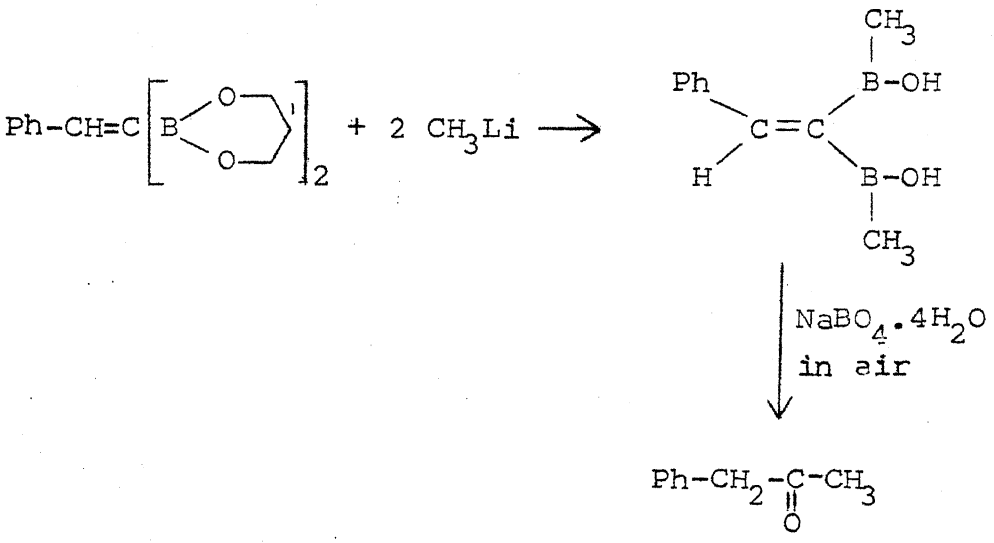


6

Treatment of 1,1-bis(trimethylenedioxyboryl)-2-phenylethene with two moles of methyllithium followed by oxidation with alkaline sodium perborate (under air) gives good yield of phenylacetone, which is the product of methyl migration from boron to carbon[19] (Scheme II.16). Examination of the reaction intermediate by ^{1}H NMR revealed that methyl migration is not brought about by water or acid and does not occur until the oxidation step. These results illustrate that structure of organoborane intermediates which contain reactive neighbouring groups cannot be assigned solely on the basis of their peroxide oxidation products.

From the previous[4,13] and above[19] results, it may be concluded that the carbon skeletons of organoboranes and thier peroxide oxidation products some time differ. Therefore, proof of the structure of organoborane intermediates based solely on

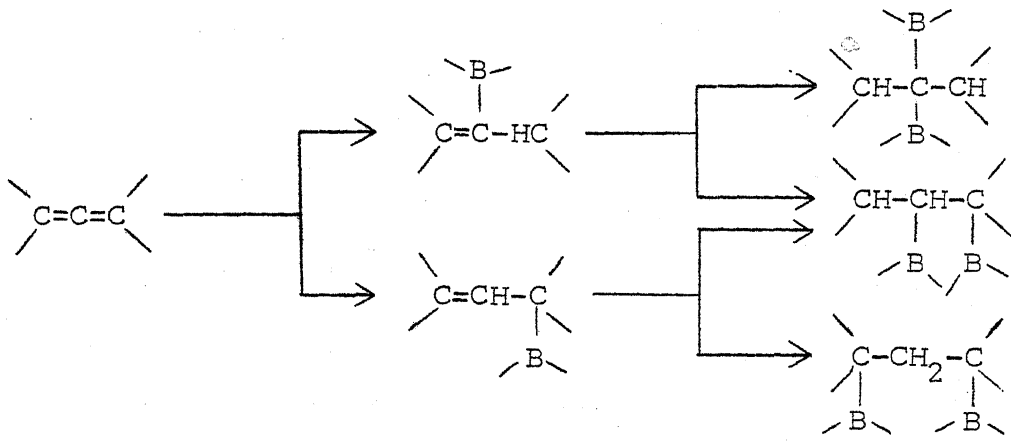
Scheme II.16



peroxide oxidation products cannot be considered valid. Of course, it is well established that ordinary alkylboranes normally give highly specific reactions with alkaline hydrogen peroxide,[20-24] but caution in interpretation seems in order wherever there are neighbouring groups, especially if quantitative significance is attached to the product distribution.

In principle, two successive cis-additions of boron hydrogen bond to two orthogonal double bonds of an allene could give rise to gem-, vic- and 1,3-diorganoboranes via vinyl and allyl organoboranes as shown in Scheme II.17. The dihydroboration of 1,2-cyclotridecadiene in tetrahydrofuran (1:1.3 mol ratio of allene:borane) followed by alkaline hydrogen peroxide oxidation gave a mixture of hydrocarbons containing cis-cyclotridecene, trans-cyclotridecene and bicyclo(10.1.0)tridecane in the ratio of 1:7:2 (5%), cyclotridecanone (1.5%),

Scheme II.17



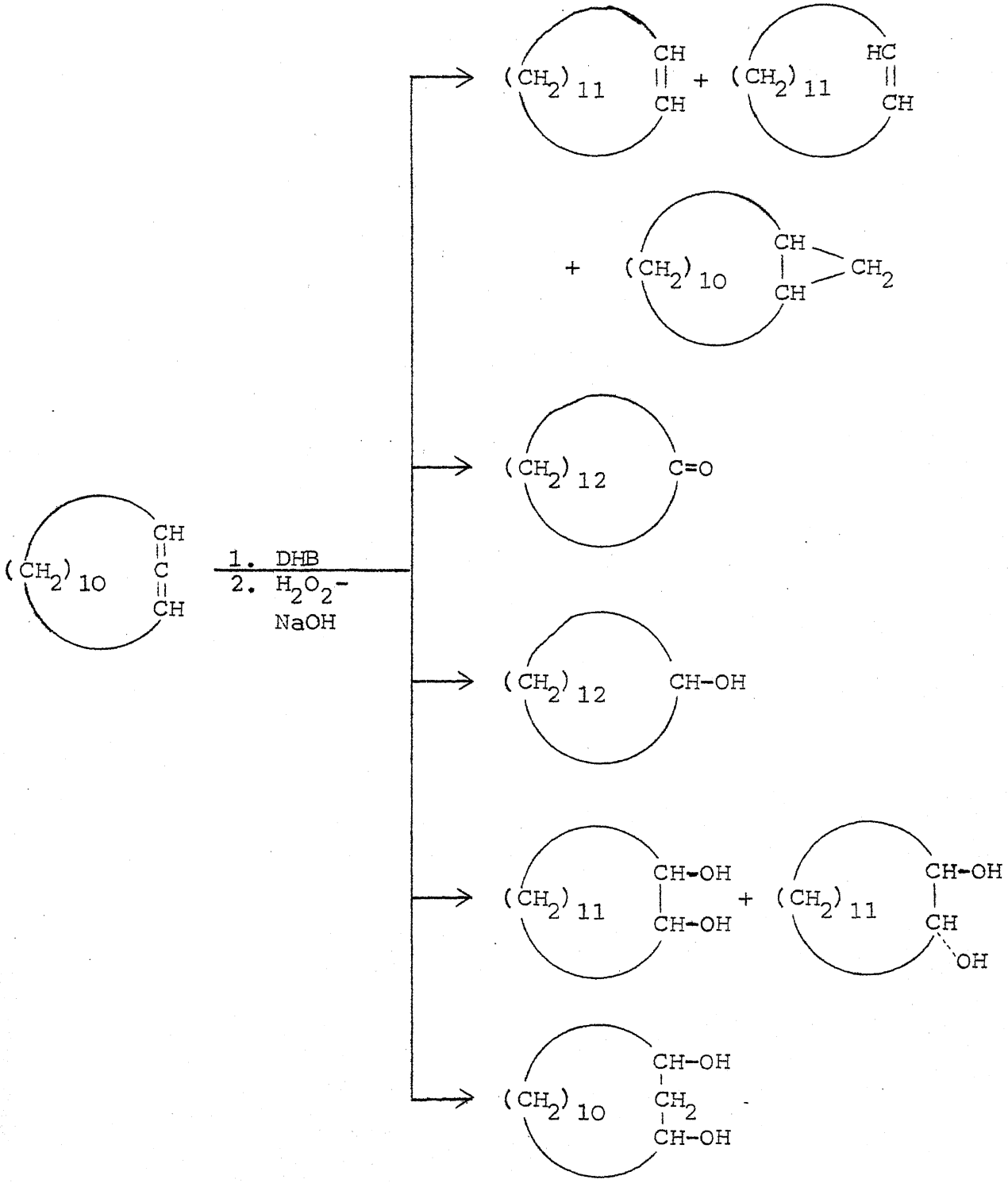
cyclotridecanol (27%), cis-1,2-cyclotridecane diol(14%), trans-1,2-cyclotridecane diol(15%) and a mixture of cis- and trans-1,3-cyclotridecane diol[25,26] (3.5%) as shown in Scheme II.18.

The formation of trans- and cis-olefins is visualised via the anion by direct elimination in accordance with Pasto's mechanism (Scheme II.19).

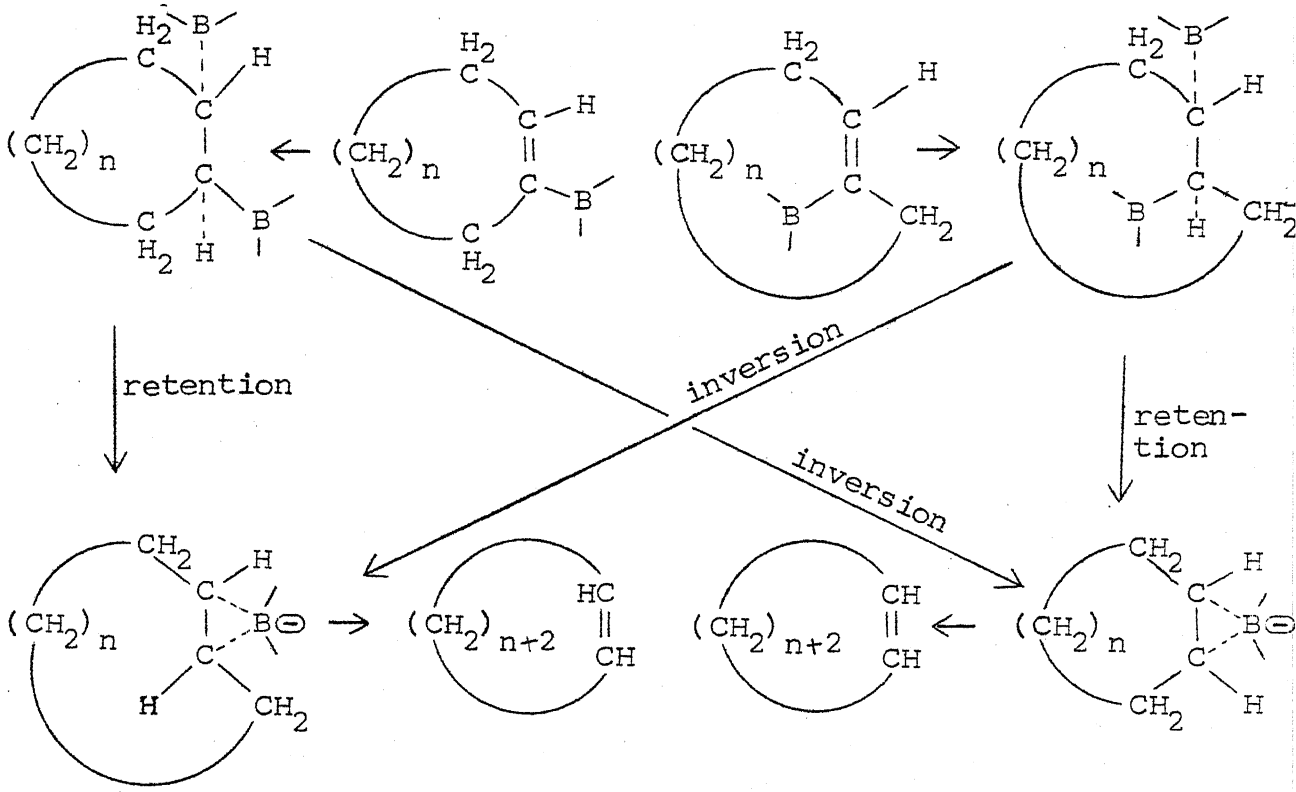
The formation of the interesting bicyclo(10.1.0)tridecane is possibly occurring from 1,3-diorganoborane via the bridged anion as shown below in Scheme II.20.

The formation of monoalcohol has been visualised by the hydrolysis of the vic-diorganoborane followed by oxidation. From the above results it can be concluded that 90% of the products are arising from 1,2-diorganoborane that is formed on dihydroboration of 1,2-cyclotridecadiene.

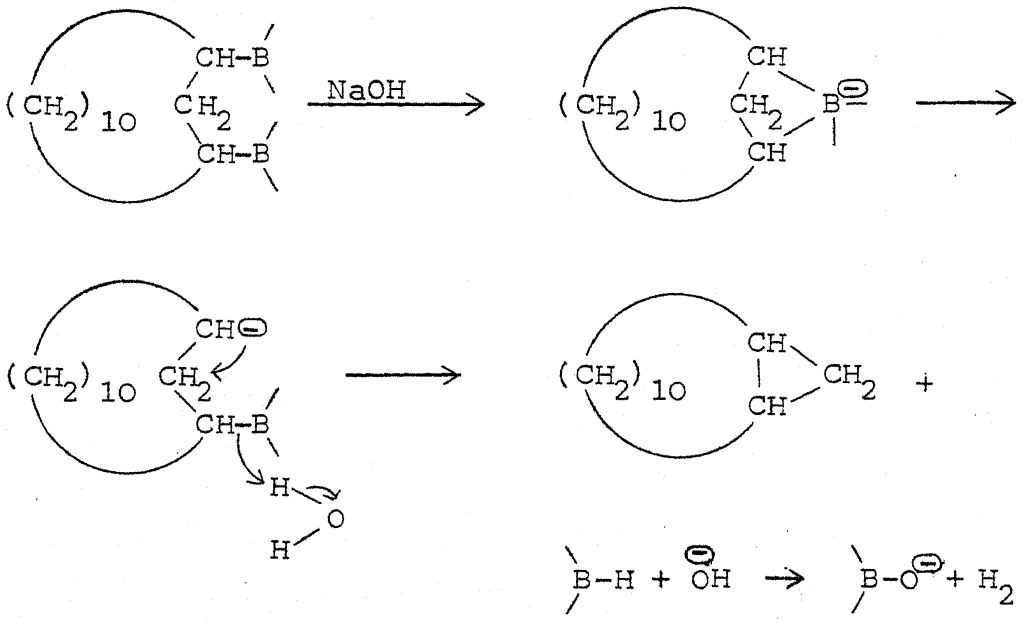
Scheme II.18



Scheme II.19

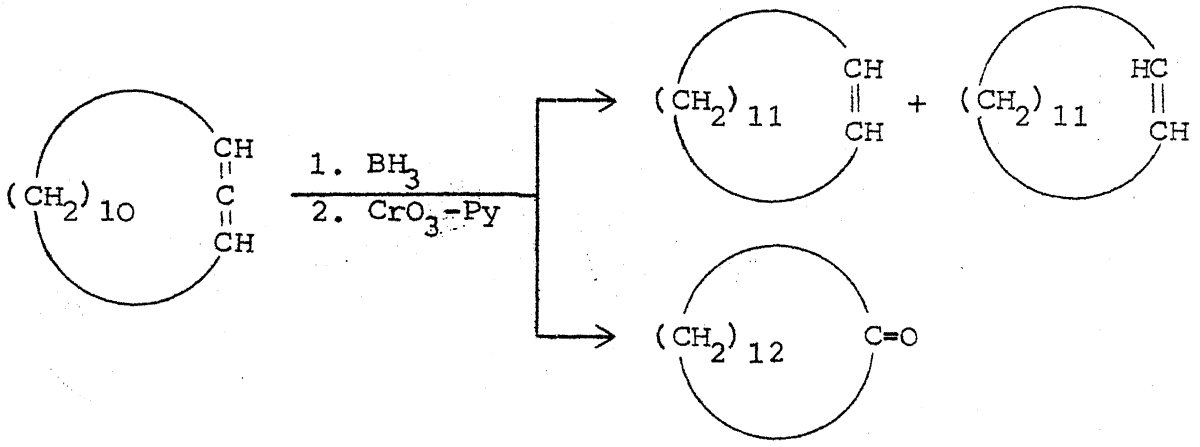


Scheme II.20



Brown and coworkers have shown that organoboranes can be converted to the corresponding ketones by chromic acid oxidation.[27] In view of this an attempt was made to synthesize 1,2-diketones by treating the various organoborane intermediates from the dihydroboration of 1,2-cyclotridecadiene. To our surprise chromium trioxide-pyridine oxidation of organoboranes gave a mixture of cis- and trans-cyclotridecenes (50%) in the ratio of 3:17 and cyclotridecanone[25] (3%) (Scheme II.21):

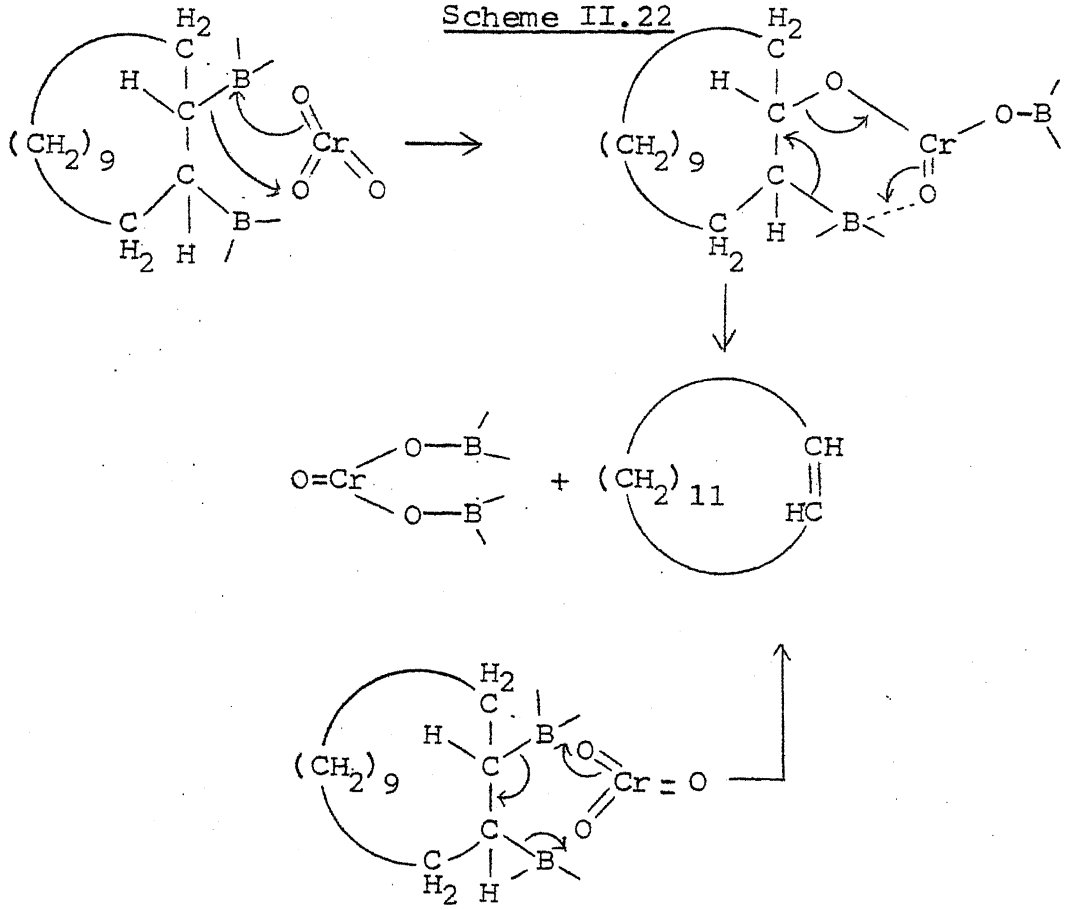
Scheme II.21



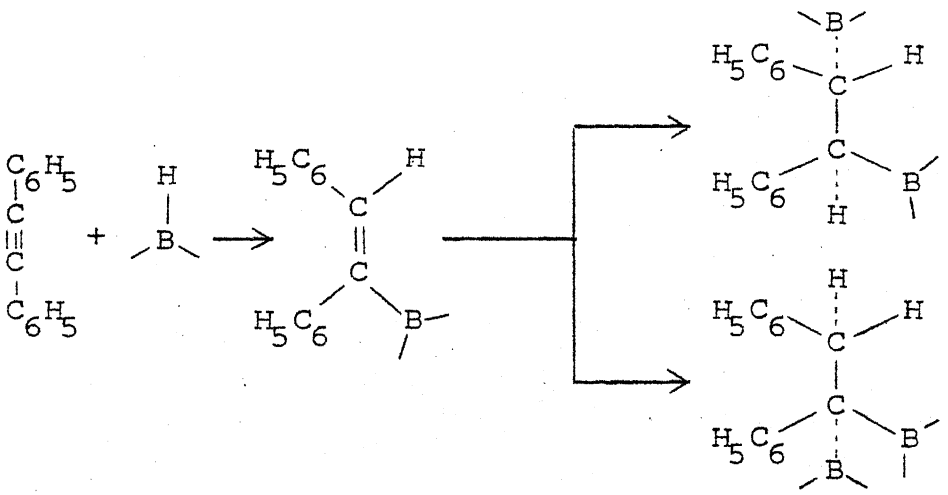
The formation of the olefinic products can be explained via a two-step or/and one step path, shown in Scheme II.22.

The substantiation or refutation of the proposed mechanism awaits the preparation of model compounds and a study of their chemistry. It is reasonable to assume that two cis-additions of >B-H bond to a carbon-carbon triple bond would lead mainly to the formation of 1,2-diorganoborane with threo configuration (Scheme II.23).

Scheme II.22

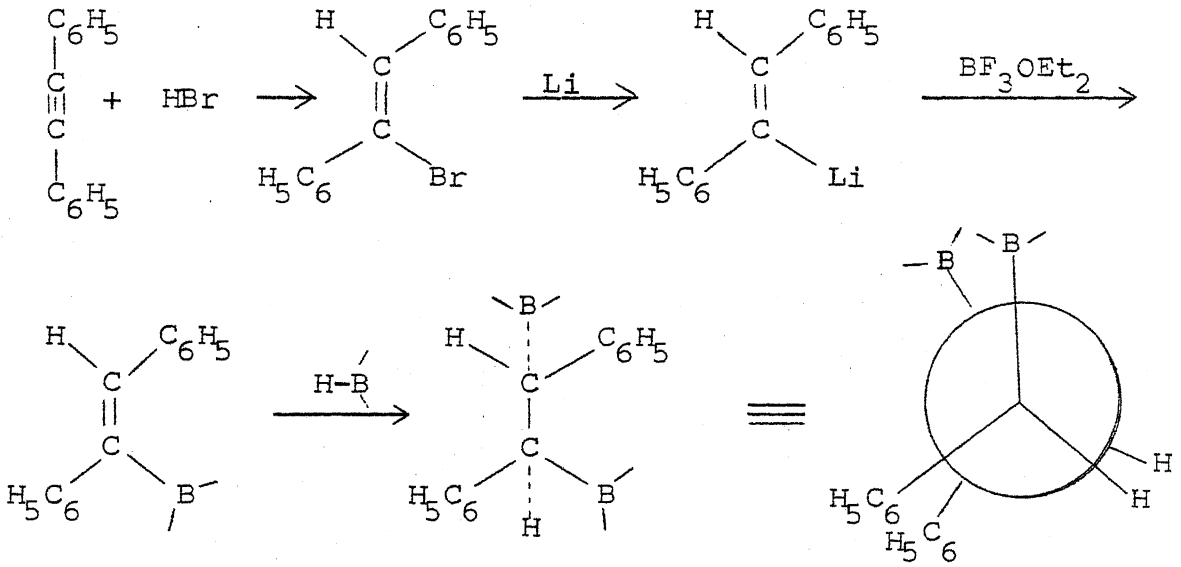


Scheme II.23



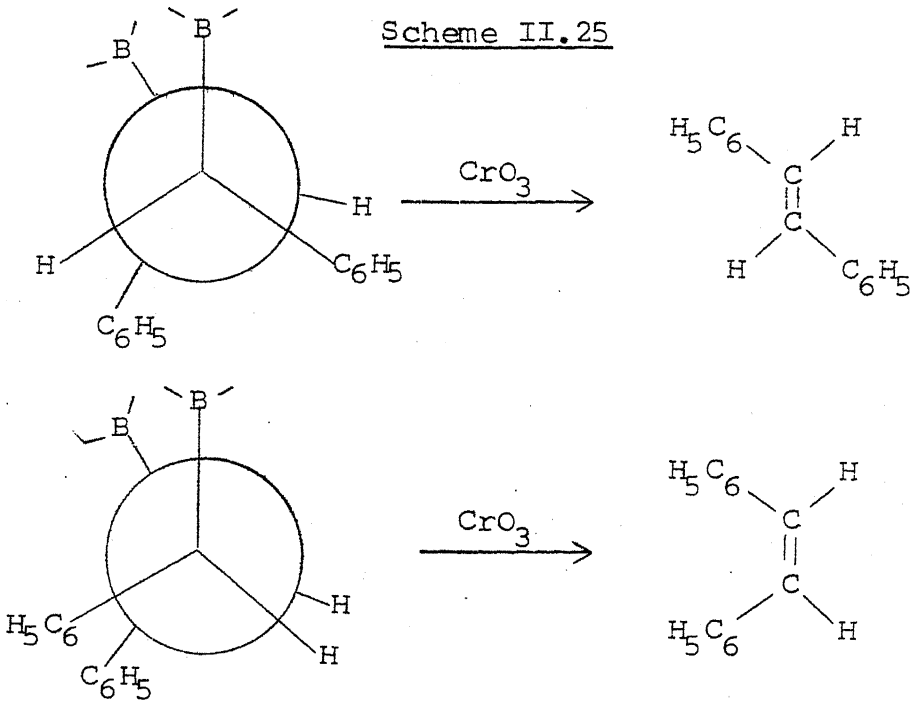
The erythro-vic-diorganoborane was synthesized from diphenylacetylene[28] (Scheme II.24). The addition of hydrogen-bromide to diphenylacetylene in 1:1 molar ratio provided trans-monobromostilbene. Treatment of alkenyllithium with boron trifluoride etherate at -30 to -35° gave the trans-vinylborane which was hydroborated as usual to get erythro-vic-diorgano-borane.

Scheme II.24



The diastereomeric vic-diorganoboranes thus synthesized were subjected to chromium trioxide-pyridine to know the stereo-chemistry of the elimination reaction. The threo-isomer gave (E)-stilbene whereas erythro-isomer gave (Z)-stilbene,[26-28] (Scheme II.25). Thus, the data demonstrates that vic-diorgano-boranes undergo elimination reaction to form olefin in cis-fashion instead of the expected oxidation to form 1,2-diketones.

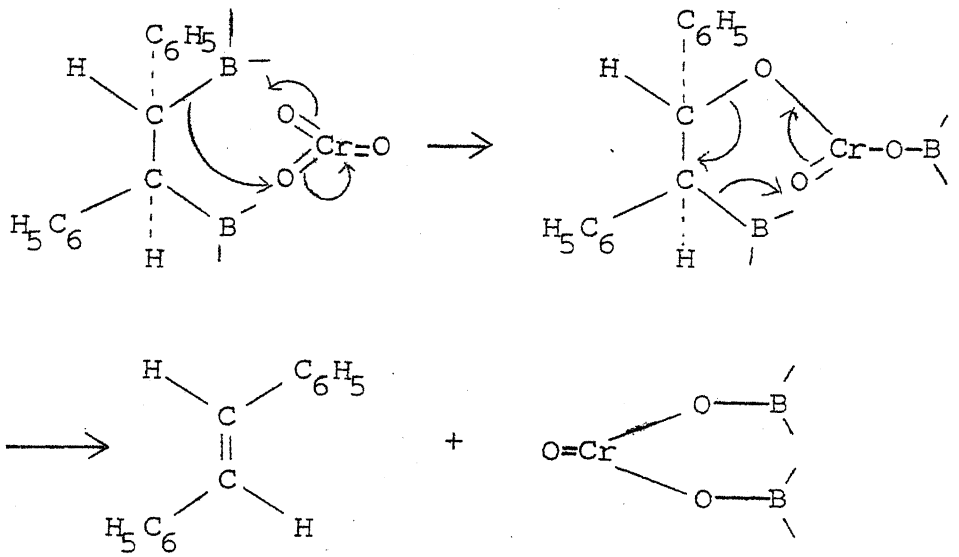
Scheme II.25



Based on these results it was suggested that a probable mechanism of this reaction could be a two-step process or a one step process. In a two step process the initial step involves breakage of chromium-oxygen d-p π-bond to form boron-oxygen bond and the intake of d-p π-electrons by chromium. This results in an intermediate with chromium ion in +4 oxidation state. The stereochemistry of the reaction can be explained as the electron deficient boron is capable of complexing with oxygen of the chromium trioxide in the intermediate. The complexed intermediate can undergo cleavage of bonds as shown in Scheme-II.26 to form (E)-stilbene.

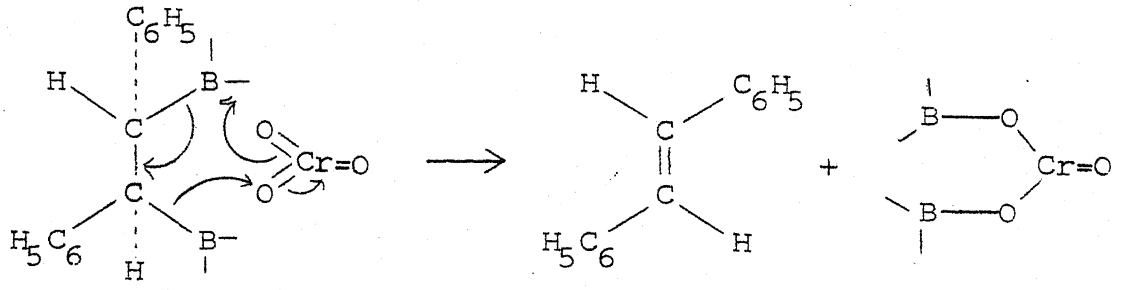
In a one-step process (concerted) the probable mechanism involves a seven membered transition state having eight electrons,

Scheme II.26



2 pairs from carbon-boron σ-bonds and two pairs from chromium-oxygen d-p π-bonds (Scheme II.27). The number of electrons in the process correspond to 4n, where n=2. Therefore, according to Woodward-Hoffmann rules, for thermally allowed process of this type the approach of the two species should be (supra-antara) or (antara-supra).[29]

Scheme II.27



The unusual reaction of vic-diorganoboranes with chromium trioxide-pyridine leading to olefins has prompted us to investigate the reaction of 1,1-diorganoboranes. Therefore, it was decided to dihydroborate a few acetylenes and treat the dihydroborated mixture of gem- and vic-diorganoboranes with chromium trioxide-pyridine.

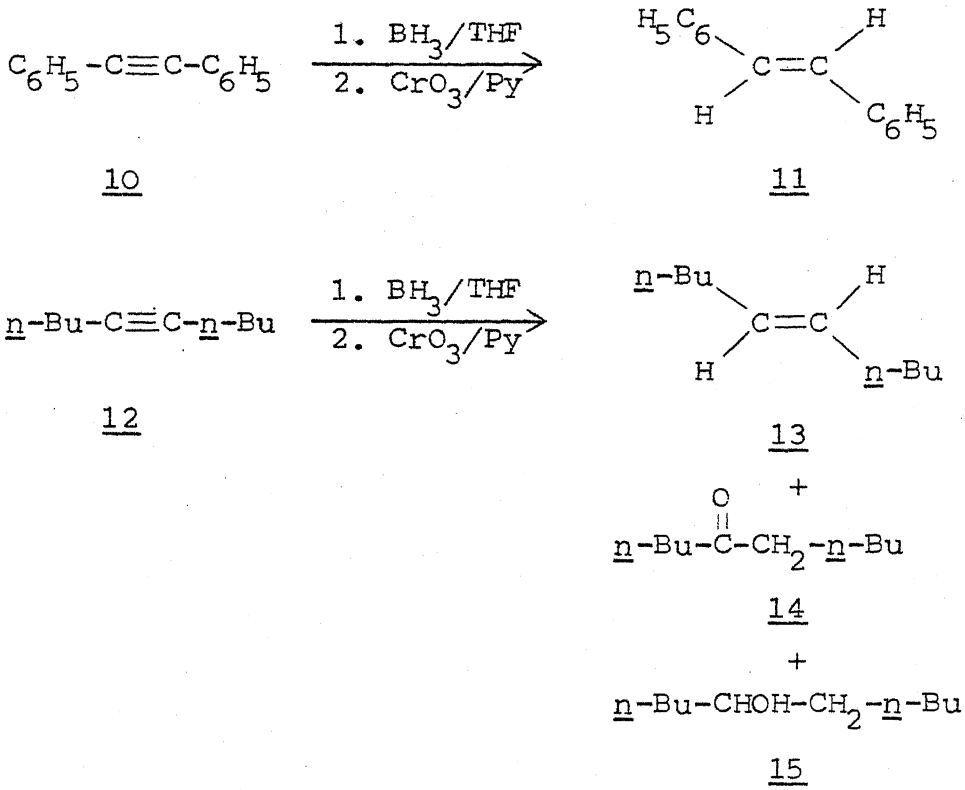
II.3 RESULTS AND DISCUSSION

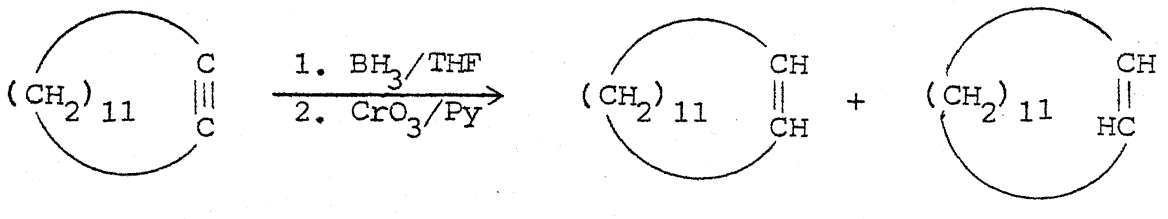
The dihydroboration reaction was carried out using standard solution of borane-tetrahydrofuran (1:2 mol ratio of acetylene: borane) in nitrogen atmosphere. The reaction mixture was stirred for 12-14 hours. The resulting organoboranes were oxidised with chromium trioxide-pyridine complex in methylene chloride and worked up in the usual manner. The mixture of products was analysed by GLC on carbowax 10' and SE-30,5' columns. The identity of the products was established by comparison of GLC retention times and IR spectra with those of authentic samples.

Diphenylacetylene (10) on dihydroboration followed by chromium trioxide oxidation yielded (E)-stilbene (11), (77%). 5-Decyne (12) under similar conditions gave (E)-5-decene (13, 54%) alongwith 5-decanone (14, 31%) and 5-decanol (15, 15%). (E)- and (Z)-cyclotridecenes (17A, 20%; 17B, 80%) were formed in 60%, when cyclotridecyne (16) was dihydroborated and treated with chromium trioxide-pyridine. Further analysis of the

crude mixture showed the presence of cyclotridecanone (18, 25%) and cyclotridecanol (19, 15%). Alkyl-aryl substituted acetylene (1-phenylpropyne, 20) also gave a mixture of (E)-1-phenylpropene (21, 62%), 1-phenyl-2-propanone (22, 30%) and 1-phenyl-2-propanol (23, 8%) (Scheme II.28). These products are formed via 1,1- and 1,2-diorganoboranes. The results of chromium trioxide-pyridine oxidation of acetylenes are listed in Table-II.3.

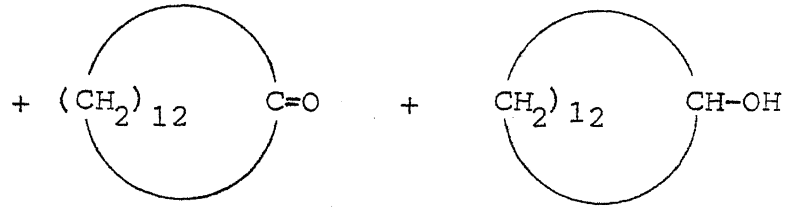
Scheme II.28



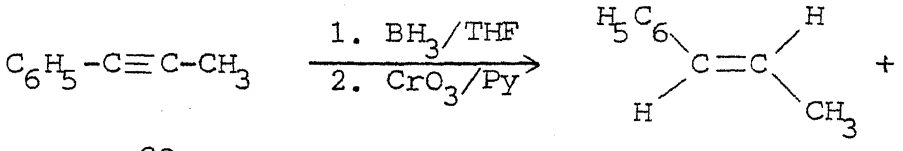


...contd.

Scheme II.28 (contd.)



18 19

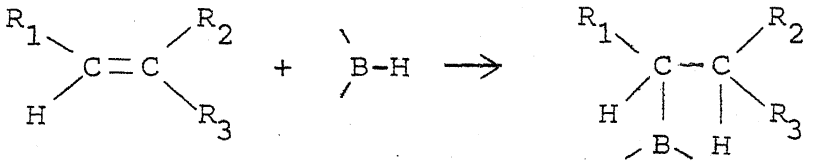


20 21

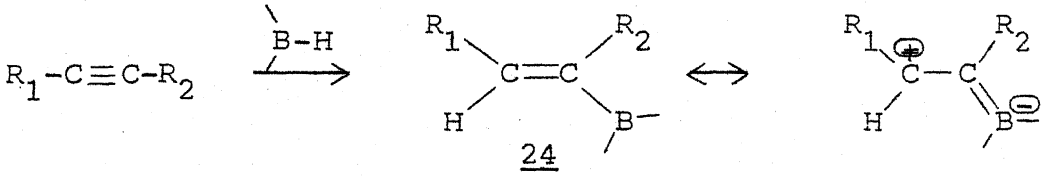
22 23

In a trisubstituted olefin the addition of $\rangle$B-H bond takes place to give 98% of the secondary derivative with only 2% of the tertiary compound.[30,31] The addition of $\rangle$B-H bond to an acetylene takes place to form a vinyl organoborane (Scheme II.29):

Scheme II.29



(98%)



24 25

But in the case of vinylorganoborane the electronic structure 25 is also significant[4] due to the participation of π-electron cloud of the double bond with vacant p orbital on the boron atom. So when R_1 and R_2 are alkyls both the structures (24, 25) are significant resulting in the formation of vic- and gem-diorganoboranes. When R_1 = Ph in structure 25 the positive charge is delocalised on the phenyl ring. This results in more of vic-diorganoborane to be formed than gem-diorganoborane. However, when R_1 and R_2 are phenyls, the phenyl group (R_2) will be out of the plane of the double bond resulting in decrease of gem-diorganoborane to be formed. Hence one expects large excess of vic-diorganoborane to be formed which happens to be the sole product.

But, however, in the case of unsymmetrical acetylene (phenyl propyne) the other organoborane 26 is possible to a considerable extent[30,31] and 26 can have resonating structures 27 and 28 (Scheme II.30). But, the cross conjugation of

Scheme II.30

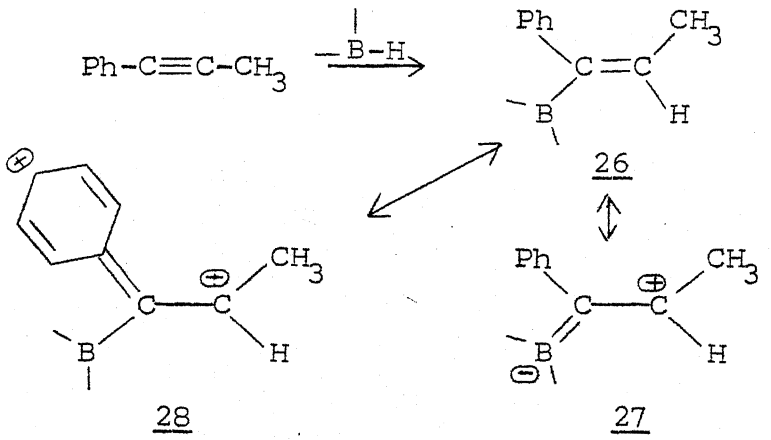


Table II.3

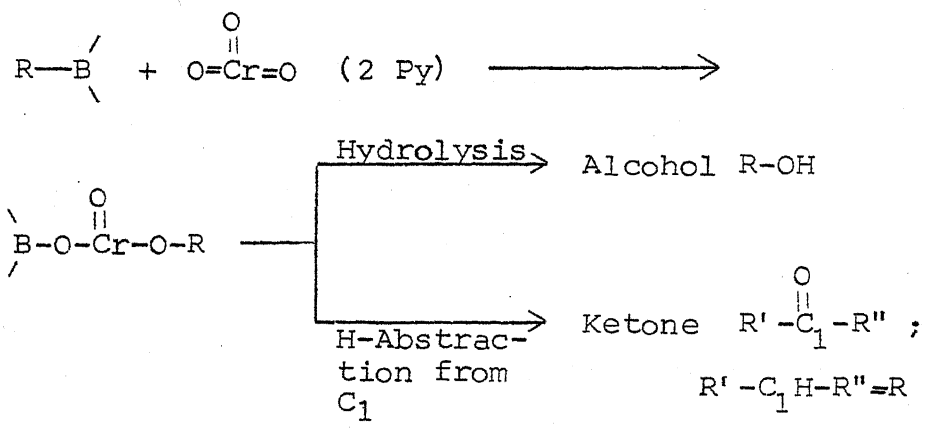
Results of Dihydroboration Followed by Chromium Trioxide-Pyridine Oxidation of Acetylenes

Acetylene	Products (%)	Yield (%)	gem (%)	vic (%)
Diphenylacetylene (10)	(E)-Stilbene (11, 100)	77	0	100
5-Decyne (12)	(E)-5-Decene (13, 54) 5-Decanone (14, 31) 5-Decanol (15, 15)	70	46	54
Cyclotridecyne (16)	(E) and (Z)-Cyclotridecene (17, 60) Cyclotridecanone (18, 25) Cyclotridecanol (19, 15)	67	40	60
1-Phenylpropyne (20)	(E)-1-Phenylpropene (21, 62) 1-Phenyl-2-propanone (22, 30) 1-Phenyl-2-propanol (23, 8)	80	38	62

phenyl is more important, resulting the contribution of 28 more than 27. Hence one expects a vic-diorganoborane to be formed. Hence one can explain the amount of gem- and vic-diorganoboranes formed from different acetylenes on dihydroboration.

The cleavage of carbon-boron bond with chromium trioxide is known to give ketone via alcohol[25,26] (Scheme II.31). Due to the participation of other boron in the molecule the course of this reaction is altered and (E)-olefins are formed from different acetylenes.

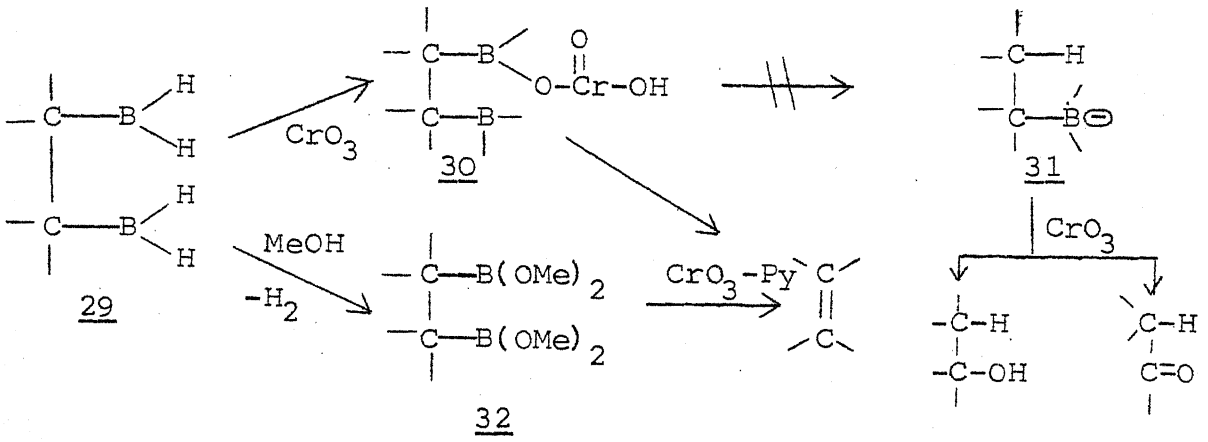
Scheme II.31



1,1-Diorganoboranes formed as intermediates on treatment with chromium trioxide-pyridine possibly lead to the corresponding ketones and alcohols in the reaction mixture. The fact that alcohol is obtained from 5-decyne (12), cyclotridecyne (16) and 1-phenylpropyne (20) indicates the hydrolysis of gem-diorganoborane to monoorganoborane followed by subsequent oxidation. It has been already suggested and established that vic-diorganoboranes undergo hydrolysis.[4] Eventually one would suspect the

formation of 5-decanone (14), cyclotridecanone (18), 1-phenyl-2-propanone (22) and 5-decanol (15), cyclotridecanol (19), 1-phenyl-2-propanol (23) from gem-diorganoboranes (Scheme II.35). In principle, the hydrolysis of vic- and gem-diorganoboranes is possible in presence of excess of hydride. Chromium trioxide

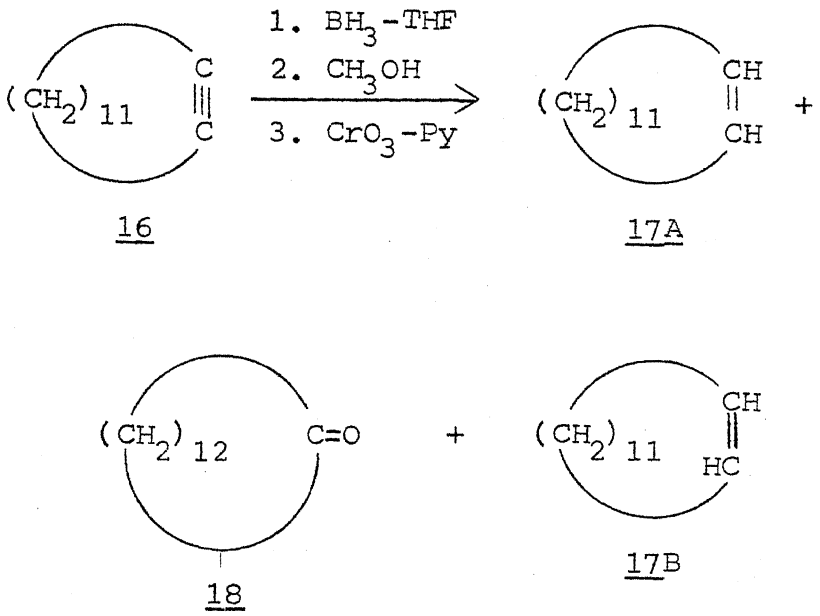
Scheme II.32



when treated with organoboranes containing $\rangle$B-H bonds, reacts relatively faster with $\rangle$B-H bond rather than boron-carbon bond. It therefore, implies that as a result of action of chromium trioxide on R-$\underset{|}{B}$-H the hydride is oxidised to proton, which can bring about the hydrolysis.

In order to check this possibility the hydroborated mixture was treated with methanol and hydrogen evolution was observed. Excess methanol was removed under vacuum. The resulting organoborane mixture containing $\rangle$B-OMe instead of $\rangle$B-H was oxidised. The oxidised mixture after usual work-up indicated olefin and ketone (Scheme II.33):

Scheme II.33

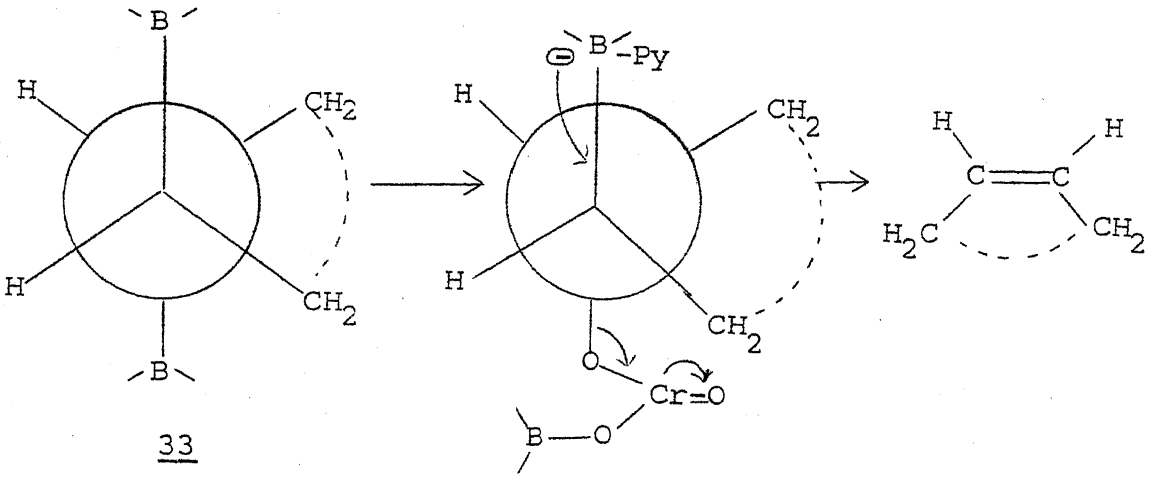


16 17A 18 17B

The fact that the amount of olefin formed does not change with or without methanol treatment of organoborane provides an evidence for the genesis of (E)-olefins from 1,2-diorganoboranes via a stereospecific cis-elimination[28] (Scheme II.27).

The small amount of (Z)-cyclotridecene present in the reaction mixture is possibly formed via trans-elimination of 1,2-diborocompound (Scheme II.34). Cyclic system alone can have conformation, 33, which is suited for trans-elimination and such a possibility is ruled out in an acyclic system. A blank experiment was carried out, where (Z)- and (E)-cyclotridecenes were treated with chromium trioxide-pyridine and worked up in the usual way. Under these conditions olefins did not change at all.

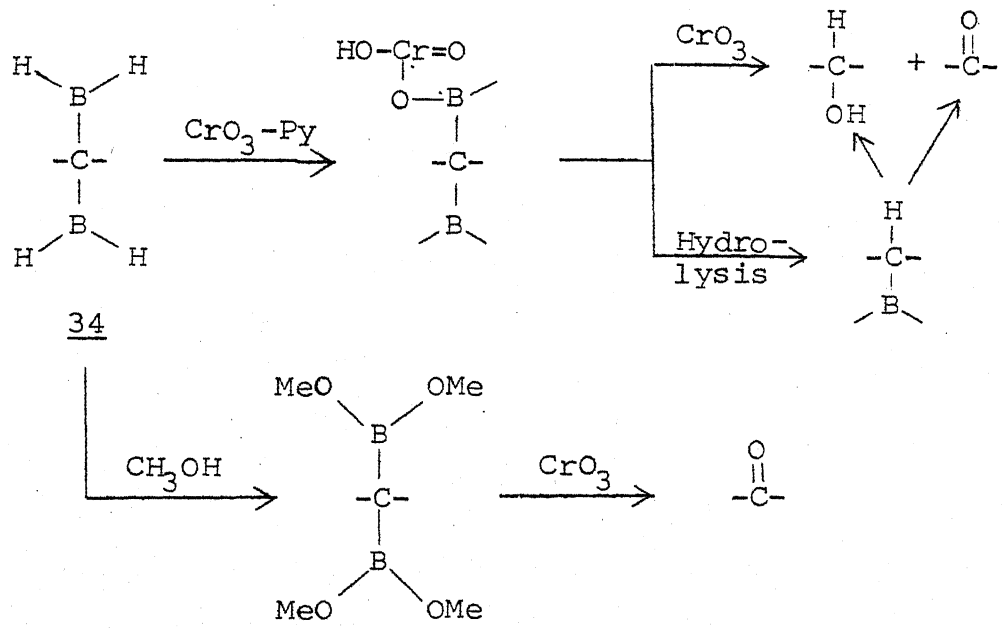
Scheme II.34



33

The carbene is not formed from 1,1-diborocompound on treatment with chromium trioxide-pyridine. This statement is substantiated by the fact that no 4-decene is obtained from the hydroboration-oxidation of 5-decyne. Evidently, 1,1-diborocompounds lead to the formation of ketones and alcohols (Scheme II.35):

Scheme II.35



34

From the above study it is evident that 1,2-diorganoborane on treatment with chromium trioxide-pyridine lead to the formation of olefins. The ketone and alcohol obtained are derived from 1,1-diorganoborane. Further, the amount of olefin isolated directly indicates 1,2-diorganoborane while ketone and alcohol put together give the amount of 1,1-diorganoborane. The relative amounts of 1,1- and 1,2-diorganoboranes obtained from different acetylenes are in good agreement with steric and electronic requirements of the parent acetylenes and intermediate monoorganoboranes.

II.4 EXPERIMENTAL

All boiling points were uncorrected. The infrared spectra were recorded on Perkin-Elmer Model 137 spectrometer as thin films. The nuclear magnetic resonance spectra were on a Varian A-60D spectrometer in carbon tetrachloride solution with tetramethylsilane as the internal standard. Gas-liquid chromatographic analyses were made with Varian Aerograph Model 90-P Instrument using 15% silicone rubber SE-30 and 15% carbowax 20M columns (60/80 mesh chromosorb-P was used as the solid support by weight). Microanalyses were performed by Mr. A.H. Siddiqui, Department of Chemistry, Indian Institute of Technology, Kanpur.

Materials

All the glassware were dried thoroughly in a drying oven and cooled under a steam of nitrogen. Boron trifluoride etherate

(BDH) was distilled over calcium hydride. Diglyme (Ansul) was distilled over lithium aluminium hydride. Tetrahydrofuran (SD) was kept over potassium hydroxide for 24 hours, refluxed over sodium wire for 6 hours and then distilled over lithium aluminium hydride. Dimethyl sulphoxide (Pfizer) was distilled over calcium hydride. Chromium trioxide (Sarabhai) was dried under vacuum for several hours and kept in a vacuum desiccator. Pyridine (Pfizer) was distilled over potassium hydroxide. Methylenedichloride was distilled over phosphorous pentoxide. Sodium was stored in high boiling hydrocarbons which could be washed with low boiling solvents like n-pentane was used. The metal was cut with stainless steel knife and freed from surface coating before use. Commercially available liquefied ammonia in steel cylinder was used. Since the ammonia gas is toxic with pungent odour, reactions using it were carried out in an efficient hood.

Preparation of Diphenylacetylene[32]

A solution of (E)-stilbene (45.0 g, 0.25 mol) in ether (750 ml) was prepared in a one litre three-necked round bottom flask fitted with a reflux condenser, an efficient mechanical stirrer and an equilibrating dropping funnel. To the well stirred solution was added bromine (43.0 g, 0.27 mol) in about 10 minutes. A solid began to separate after 5 minutes, but stirring was continued for one hour. The product was filtered and washed with ether until the solid became white. The yield

of stilbenedibromide (63.0 g, 0.185 mol) was 74% m.p. 235-237°.

A solution of potassium hydroxide (90 g, 1.6 mol) in absolute ethanol (150 ml) was prepared in a 500 ml two-necked round bottom flask fitted with a reflux condenser. A complete dissolution of alkali in alcohol was effected by refluxing the alcohol for some time. Since the addition of dibromide causes an immediate vigorous reaction, the solution was cooled and the dibromide (63.0 g, 0.19 mol) was added in several small portions. The mixture was then refluxed for 24 hours. The hot mixture was poured into cold water (750 ml) with stirring. The diphenylacetylene formed was filtered, washed completely free of alkali and dried to obtain diphenylacetylene (30.5 g, 0.17 mol) in 89% yield, m.p. 58-60°. The crude product was recrystallised from 95% ethanol (50 ml) to get diphenylacetylene (24.0 g, 0.14 mol) in 56% yield (based on stilbene), m.p. 60° (lit.[33] m.p. 59-61°).

Anal. for $C_{14}H_{10}$: Calcd C, 94.39; H, 5.61.
Found C, 94.31; H, 5.42%.

Preparation of 5-Decyne[34]

Preparation of Sodamide

To a mechanically stirred mixture of finely powdered ferric nitrate (0.3 g) in liquid ammonia (400 ml) contained in a one litre three-necked flask equipped with an ethanol-liquid nitrogen condenser, mechanical stirrer and an inlet for ammonia gas , sodium (1 g) was added, air was bubbled through the solution until the blue colour was discharged. Sodium (18.4 g, 0.8 g.atom)

was added in small lumps and the mixture was stirred for half an hour during which the blue colour was replaced by grey.

Preparation of Sodium Acetylide in Liquid Ammonia

In a two litre four-necked flask, equipped with ethanol-liquid nitrogen condenser, an inlet for ammonia and acetylene gas, a mercury sealed mechanical stirrer and the fourth was meant for adding sodium, liquid ammonia (500 ml) was condensed. The ammonia gas inlet was replaced by a long gas inlet tube which dipped below the surface of liquid ammonia and acetylene was bubbled through ammonia at a very rapid rate that entire solution never became blue. A slow stream of acetylene was bubbled continuously during this period. The entire addition took half an hour. The mixture was stirred for additional 15 minutes.

Sodamide (0.8 mol) in liquid ammonia prepared as above was then added rapidly into the sodium acetylide mixture. The mixture was stirred for 0.5 hour, n-butylbromide (137 g, 1 mol) was added slowly during the course of two hours with vigorous stirring. Stirring was continued for additional three hours and then water (500 ml) followed by petroleum ether (40-60^{o}) (200 ml) were added slowly. Organic layer was separated immediately, washed with water, dilute hydrochloric acid, again with water, then with dilute sodium bicarbonate solution and finally with distilled water. The solution was dried over calcium chloride (anhydrous), solvent was removed at atmospheric

pressure using long fractionating column. The crude product was distilled using a 15 cm vigreux column to give 5-decyne (46 g, 0.34 mol) in 67% yield, b.p. 90-92°/49 mm (lit.[34] 104-106°/79 mm).

NMR : δ2.37-1.76 (4H, m); 1.76-1.16 (8H, m); 1.16-0.66 (6H, m).

IR : 2210 cm^{-1}.

GLC analysis indicated it to be 98% pure.

Preparation of Cyclotridecyne[35]

1,2-Cyclotridecadiene (14 g, 0.08 mol) was added to a solution of potassium t-butoxide (17.9 g, 0.16 mol) in dry dimethylsulphoxide (80 ml) and allowed to stir for 24 hours at 30° under nitrogen atmosphere. The excess base was destroyed by quenching the reaction with water (200 ml) and extracting the reaction mixture with ether (150 ml). The ethereal solution was washed with dilute hydrochloric acid (5%), sodium bicarbonate (5%), water and then dried over anhydrous magnesium sulphate. Removal of the solvent gave a light yellow liquid which was distilled under vacuum to give cyclotridecyne (12 g, 0.067 mol) in 84% yield, b.p. 84-86°/3 mm (lit.[35] 84-86/3 mm).

NMR : δ2.13 (4H, s), 1.4 (18 H, s).

Anal. for $C_{13}H_{22}$: Calcd C, 87.6; H, 12.40.
Found C, 87.2; H, 12.13%.

GLC analysis indicated it to be 96% pure.

Preparation of Phenylpropanone[36]

A mixture of phenylacetic acid (54.4 g, 0.40 mol), acetic anhydride (200 ml) and dry pyridine (200 ml) was refluxed for 6 hours, during first part of which time CO_2 evolution was vigorous. Solvent was removed under reduced pressure and the residue was taken up in benzene and shaken out with sodium hydroxide (60%). After washing with water, the benzene layer was dried on anhydrous sodium sulphate. Removal of benzene left out a dark brown product which was distilled under vacuum to give phenylpropanone (32 g, 0.24 mol) in 58% yield, b.p. 48-50°/0.5 mm (lit.[37] b.p. 97-98.5°/13 mm).

GLC analysis on SE-30 showed it to be 98% pure.

IR: 1700 cm^{-1} ($\nu C=O$).

Preparation of 1-Phenylpropyne[38]

In a two necked 500 ml round bottom flask, fitted with a dropping funnel and a condenser the outlet of which leading to a mercury bubbler, was taken phosphorous pentachloride (56.5 g, 0.27 mol), phenylpropanone (31.0 g, 0.225 mol) was added slowly with intermittent shaking and cooling to moderate the temperature. After the addition was over the contents were heated for four hours at 110°. Phosphorous oxychloride was distilled off at 5 mm at room temperature. The residue was distilled to give mixture of chloroalkenes (28.5 g, 0.19 mol) in 83% yield.

Over a period of 2 hours the mixture of isomeric chloroalkenes (28 g, 0.19 mol) was added carefully to a refluxing mixture of potassium hydroxide (40.8 g, 0.73 mol) in absolute ethanol (100 ml). An immediate precipitation of potassium chloride and appearance of deep orange colour were signs of a positive reaction. After additional seven hours the reaction mixture was quenched with water and then extracted with benzene, washed with water and dried over anhydrous magnesium sulphate. Removal of the solvent and distillation of the product gave 1-phenyl propyne (16 g, 0.14 mol) in 74% yield, b.p. 48-54°/3 mm (lit.[39] b.p. 70-78°/10 mm).

NMR: δ7-7.5 (5H, m); 1.82 (3H, s).

IR : 2250 cm^{-1} ($\nu \equiv C-CH_3$).

GLC analysis indicated it to be 97% pure.

General Procedure for Dihydroboration of Acetylenes

A 250 ml three-necked round bottom flask fitted with a pressure equilibrated dropping funnel, an inlet and outlet for nitrogen gas was cooled with an ice-salt mixture bath. Appropriate acetylene (10 mmol) dissolved in dry tetrahydrofuran (15 ml) was transferred to the flask. BH_3-THF (2M, 10 ml, 20 mmol) was added over a period of 0.5 hour and the dropping funnel was rinsed with tetrahydrofuran (5 ml) to ensure quantitative borane addition. The reaction mixture was stirred for 4 hours at 0° and then for 12 hours at room temperature.

General Procedure for Chromium Trioxide-Pyridine Oxidation of Dihydroboration Product from Acetylenes

A solution of chromium trioxide-pyridine complex was obtained by adding chromium trioxide (5 g, 50 mmol) to a magnetically stirred solution of pyridine (8.7 g, 110 mmol) in methylenedichloride (200 ml). The solution was added to the organoboranes from appropriate acetylenes in 0.5 hour and the reaction mixture was stirred for 6 hours. Solvent ether (300 ml) was added and mixture was allowed to stir for 10 minutes and filtered. The filtrate was washed with dilute sodium hydroxide (10%), dilute hydrochloric acid (5%), water, sodium bicarbonate, again with water till neutral and dried over anhydrous magnesium sulphate. The solvent was removed by distillation to give the products.

Dihydroboration-Oxidation (Chromium Trioxide-Pyridine) of Diphenylacetylene

Diphenylacetylene (1.80 g, 10 mmol) was hydroborated with borane in tetrahydrofuran (2M, 10 ml, 20 mmol). To this, a solution of chromium trioxide-pyridine complex obtained by adding chromium trioxide (5.0 g, 50 mmol) and pyridine (11.8 g, 150 mmol) in methylenedichloride (200 ml) was added. After the usual work-up, it gave (E)-stilbene (1.38 g, 0.77 mol) in 77% yield, m.p. and mix m.p. was 125°. (E)-Stilbene was recrystallised from ethanol.

Dihydroboration-Oxidation (Chromium Trioxide-Pyridine) of 5-Decyne

5-Decyne (1.50 g, 11 mmol) was hydroborated in the usual way and oxidised using chromium trioxide (5.0 g, 50 mmol) and pyridine (11.8 g, 150 mmol). The usual work-up of the reaction mixture yielded a substance (1.05 g, 70%), b.p. 60-80°/5 mm. GLC analysis of the distilled product on a carbowax column showed the presence of (E)-5-decene, 5-decanone and 5-decanol in the ratio of 54:31:15. Pure compounds were obtained by preparative GLC and characterised by comparison of IR with those of authentic samples.

Dihydroboration-Oxidation of Cyclotridecyne

Following the general procedure, cyclotridecyne (1.78 g, 10 mmol) was hydroborated and oxidised. The usual isolation procedure gave a mixture of products (1.20 g, 67%), b.p. 82-106°/2 mm. The distilled material showed four peaks on SE-30 column. Pure compounds were isolated by preparative GLC and identified to be (Z)- and (E)-cyclotridecenes (20:80). Cyclotridecanone and cyclotridecanol in the ratio of 60:25:15. The pure components were separated by preparative GLC and identified by comparison of IR with those of authentic samples.

Dihydroboration-Oxidation of 1-Phenylpropyne

1-Phenylpropyne (2.32 g, 20 mmol) was dihydroborated and oxidised using chromium trioxide (10 g, 100 mmol) and pyridine

(23.6 g, 300 mmol) to get a product (1.84 g, 80%), b.p. 51-60°/ 35 mm and 80-86°/2 mm. GLC analysis of the mixture on a carbowax column revealed the presence of (E)-1-phenyl-1-propene, 1-phenyl-2-propanone and 1-phenyl-2-propanol in the ratio of 62:30:8. The pure components were separated by preparative GLC and identified by comparison of IR with those of authentic samples.

Dihydroboration-Methanol Treatment-Oxidation of Cyclotridecyne

Cyclotridecyne (1.78 g, 10 mmol) was hydroborated, methanol was added to destroy the residual hydride. Tetrahydrofuran and methanol were removed under vacuum at room temperature in nitrogen atmosphere. The organoborane thus obtained was oxidised in the usual manner using chromium trioxide (5 g, 50 mmol) and pyridine (11.8 g, 150 mmol), after usual work-up procedure gave the product (1.20 g, 67%), b.p. 70°/0.25 mm. The GLC analysis of the distilled product showed (Z) - & (E)-cyclotridecenes and cyclotridecanone in the ratio (11:44:45). The pure components were separated by prepative GLC and identified by comparison of IR with those of authentic samples.

Dihydroboration-Oxidation (Excess of Chromium Trioxide-Pyridine) of Cyclotridecyne

Following the general procedure cyclotridecyne (1.78 g, 10 mmol) was hydroborated with BH_3-THF (2.6 M, 10 ml, 20 mmol) in tetrahydrofuran. After stirring for 4 hours at 0° and 12 hours at room temperature the organoborane was oxidised with

excess of chromium trioxide-pyridine complex obtained by adding chromium trioxide (10 g, 100 mol) in pyridine (23.6 g, 300 mmol) in methylenedichloride (300 ml). The usual isolation gave the product (1.2 g, 67%), b.p. 71°/0.25 mm. Careful GLC analysis on 6' SE-30 column showed the presence of cis & trans-cyclotridecenes(54%) in the ratio of 19:81 and cyclotridecanone (46%).

Dihydroboration and Hydride Activity Measurement

1-Phenylpropyne (1.16 g, 10 mmol) in dry tetrahydrofuran (10 ml) was taken in a 100 ml three-necked flask equipped with a dropping funnel, an inlet and outlet for dry nitrogen gas. The flask was immersed in an ice-salt bath and BH_3-THF (2.2 M, 10 ml, 20 mmol, 0.066 mol hydride) was added through the dropping funnel over a period of 30 minutes at 0°. It was allowed to stir for 4 hours at 0° and then 12 hours at room temperature. Methanol was added carefully through the dropping funnel and the evolved hydrogen was measured carefully. After stirring for another 1 hour there was obtained 1170 ml of hydrogen.

Amount of hydride taken = 0.066 mol

Volume of H_2 evolved = 1170 ml
= 0.047 mol of hydride

Therefore amount of hydride consumed = 0.019 mol.

II.5 REFERENCES

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CHAPTER III

OXIDATION OF ORGANOBORANES WITH PYRIDINIUM CHLOROCHROMATE : A FACILE SYNTHESIS OF KETONES FROM ALKENES[1]

III.1 ABSTRACT

Organoboranes from cyclohexene, cycloheptene, (Z)-cyclooctene, (Z)-cyclononene, (Z)-cyclodecene, (Z)-cyclododecene and (E)-4-octene on oxidation with an excess of pyridinium chlorochromate in methylene chloride provide ketones in 81-92% yield. We believe that the oxidation of organoboranes with pyridinium chlorochromate proceeds *via* the formation of borate esters which subsequently get oxidized to the ketones. The anhydrous reaction conditions and easy work-up procedure employed in this reaction, thus make it a convenient one step procedure for the oxidation of alkenes to ketones in high yield.

III.2 INTRODUCTION

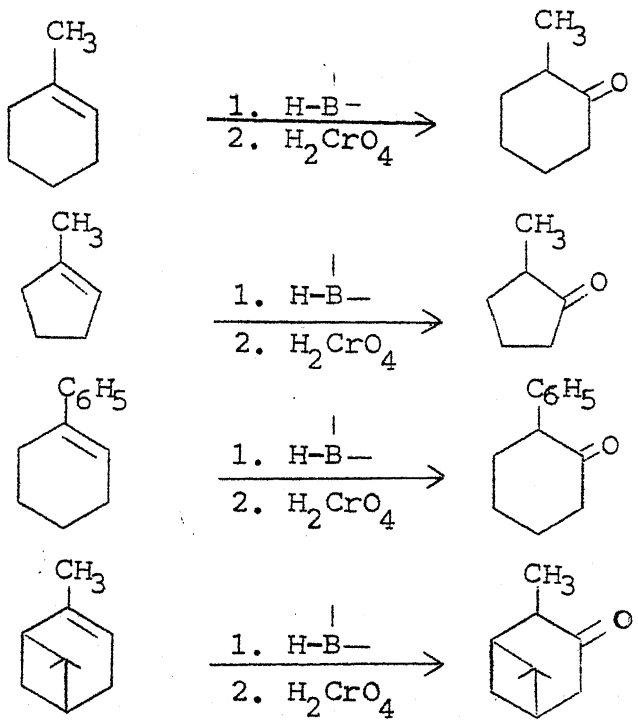
The vast utility of organoboranes in synthetic organic chemistry[2-5] is due to two reasons. First is the ready availability of organoboranes by the addition of B-H to different

kinds of unsaturated functional groups under very mild conditions. Second is the diverse reactions exhibited by organoboranes with different kinds of oxidizing agents to form alcohols, aldehydes, ketones, glycols or hydroperoxides without affecting the basic skeleton of the molecule in majority of cases.

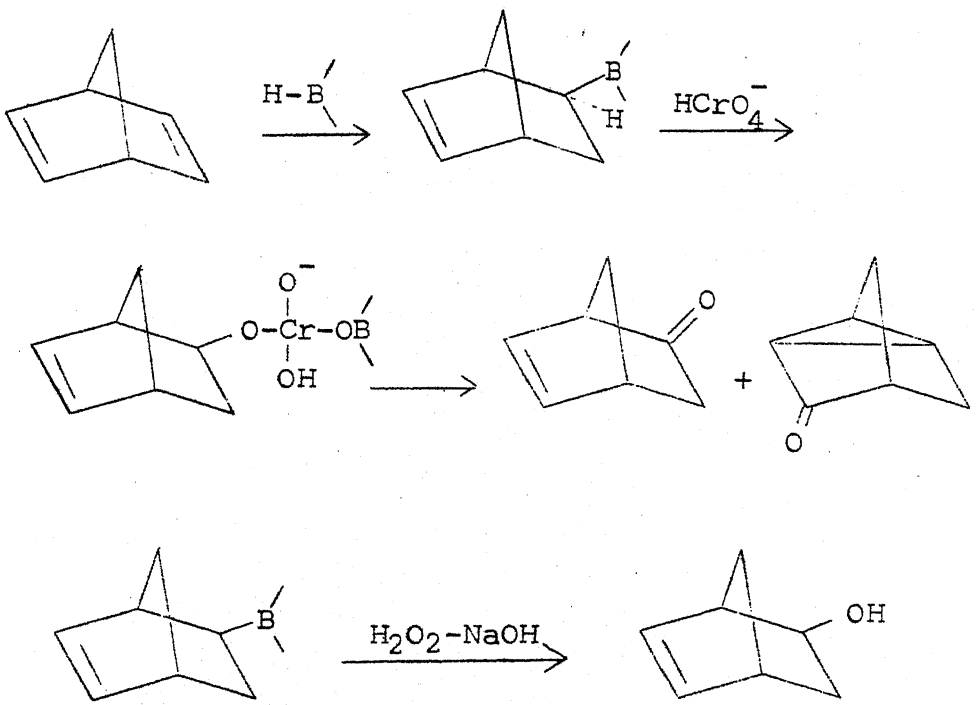
Brown and Garg[6] were interested in the direct oxidation of organoboranes to ketones instead of a two-step conversion via alcohols. Therefore, chromic acid which is the preferred reagent for the conversion of secondary alcohols to ketones,[7] was selected as the oxidizing agent to produce ketones from organoboranes. In a typical experiment the hydroboration was carried out in solvents like tetrahydrofuran or diglyme or diethylether. A small quantity of water was added to destroy the excess of hydride. To this was added an excess of 10% aqueous chromic acid at 25-35^{o} and the contents were stirred for 2 hours. Ketones were obtained as products in yields ranging between 65-85% (Scheme III.1). Brown and coworkers[8,9] also developed a convenient procedure to convert secondary alcohols to ketones in excellent yields utilizing aqueous chromic acid in diethylether.

For the first time Lansbury and Nienhouse[10] observed the formation of two isomeric ketones in the ratio of 1:1 during partial hydroboration and chromic acid oxidation of norbornadiene (Scheme III.2). They also found that if the intermediate organoborane was oxidized by alkaline hydrogen peroxide and then with aqueous chromic acid, the expected ketone was the only product.

Scheme III.1



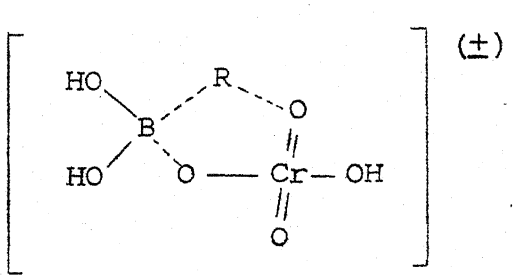
Scheme III.2



The control experiment suggests that the rearrangement occurs prior to the formation of alcohol. The observed rearrangement (Wagner-Meerwein) is similar to the one that is encountered during the solvolysis of norbornenyl tosylates. It was thought by these workers that rearrangement product could arise by C-O bond homolysis in the intermediate Cr(IV) ester (Scheme III.2). The ionic mechanism was however, ruled out because it could not explain the absence of detectable p-anisyl migration in the deutereoboration-oxidation of trans-2-p-anisyl-2-butene. Hence, it has been suggested[10] that C-O cleavage may occur by homolysis although the presence of added oxygen or manganese(II) ions did not effect the reaction appreciably.

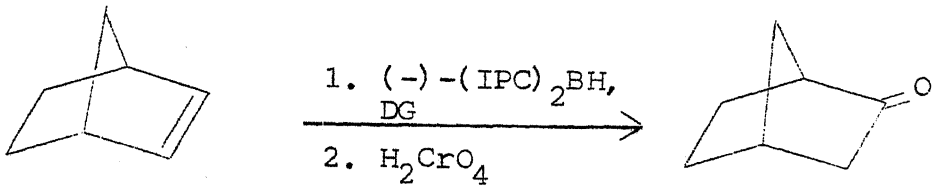
Kinetic study on the oxidation of alkylboronicacid using chromic acid has been examined by Ware and Traylor[11] over a wide range of pH. Between pH 3 to 7 where alcohols are fairly stable to Cr(VI) species, it would be possible to synthesize alcohols by oxidation of organoboranes with chromic acid. The reaction rate is quite sensitive to the structure of migrating group, in contrast to that of oxidation by alkaline hydrogen peroxide. Hence, the following transition state has been proposed (Scheme III.3) :

Scheme III.3



The reaction of norbornene with (-)-diisopinocamphenylborane followed by chromic acid oxidation, gives (1S,4R)-(+)-norcamphor of 21% optical purity in 27% yield[12] (Scheme III.4):

Scheme III.4



(27%) 21% optical purity

Selective oxidation of large ring organoboranes with chromic acid[13] has been used for the synthesis of macrocyclic musk compounds (Scheme III.5). The product distribution from varied amounts of diborane are indicated in Table III.1. The yields were based on GLC analysis utilizing an internal standard.

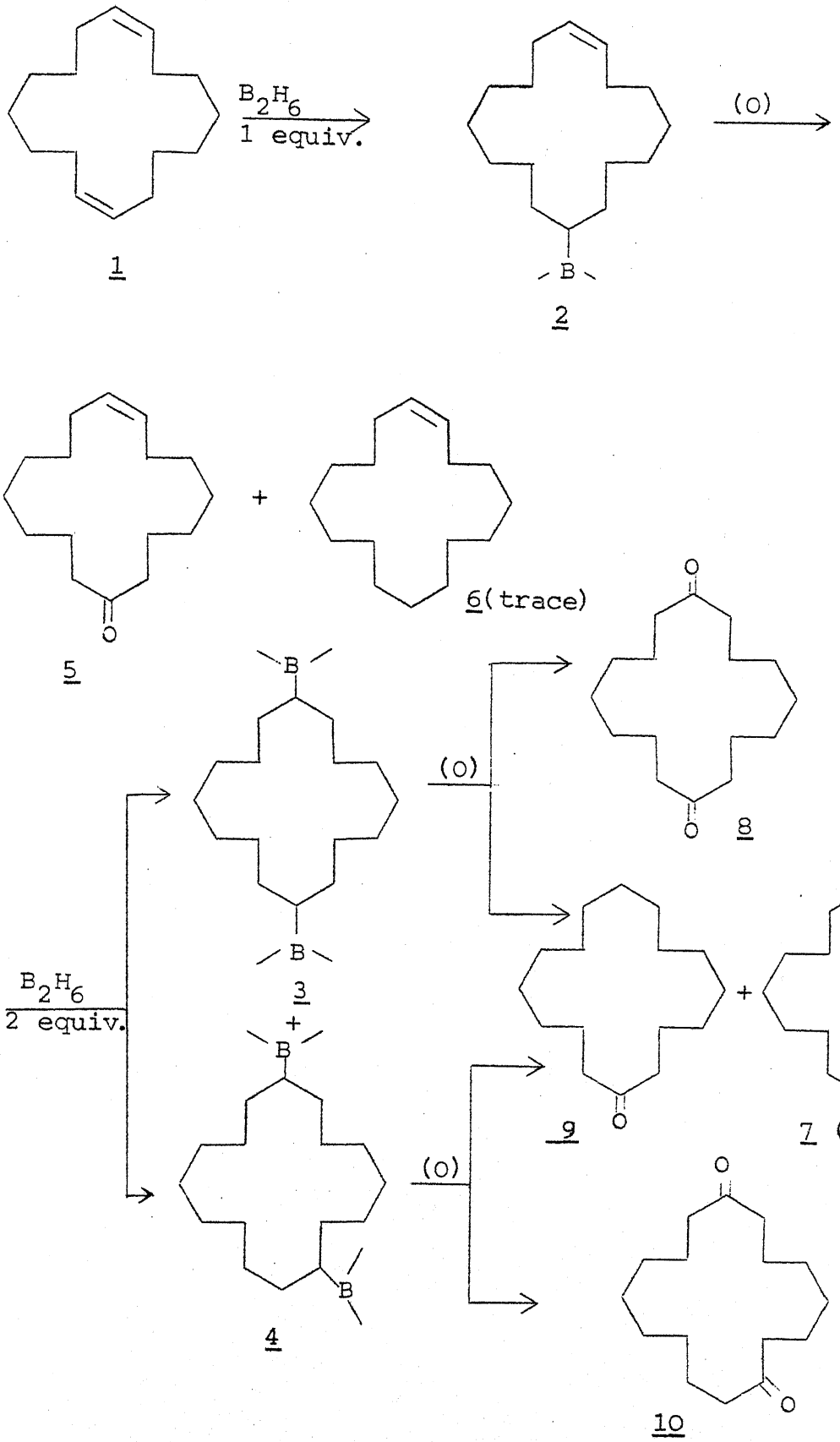
Table III.1

Product Distribution from Varied Amounts of Diborane

Diborane diene, equiv.	%5	%9	%(8 and 10)[a]
1	44	1	4
2	26	19	44
3	20	26	45

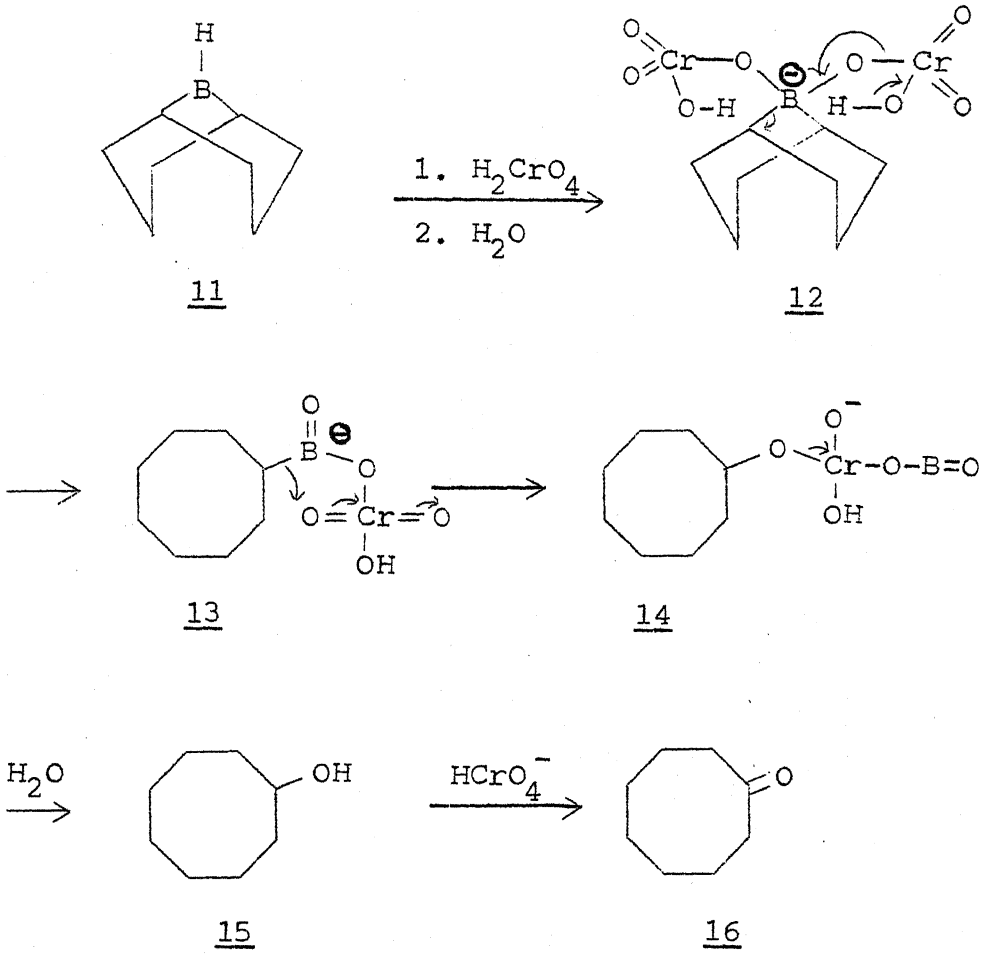
a. The diketones were shown by GLC analysis to be in equal amounts.

Scheme III.5


B2H6
1 equiv.
(O)
1
2
5
+
6(trace)
B
B
3
+
B
B
4
1
B2H6
2 equiv.
(O)
8
O
O
(O)
9
+
7 (trace)
O
O
10
O

Bicyclic organoboranes 9-borabicyclo[3.3.1]nonane, 10-borabicyclo[4.3.1]decane and 11-borabicyclo[5.3.1]undecane on oxidation with an excess of aqueous chromic acid gave monocyclic ketone[14] in 60-65% yield. The possible pathway for the formation of cyclooctanone (16) from 9-borabicyclo[3.3.1]nonane (11) is represented in Scheme III.6. Reaction of 11 with aqueous chromic

Scheme III.6



11 12 13 14 15 16

acid initially gives 12. The organoborane 12 could then undergo protonolysis of the carbon-boron bond either through an intramolecular six membered cyclic transition state or by an inter-

molecular process. (The driving force for such a reaction could be the greater strength of boron-oxygen bonds as compared to boron-carbon bonds.) Such a protonolysis of 12 would give 13, which could undergo normal chromic acid oxidation via 14 and cyclooctanol (15) to give cyclooctanone (16).

Pyridinium chlorochromate (PCC), a readily available, stable oxidizing agent, converts a wide variety of alcohols to carbonyl compounds with high efficiency.[15] It is easily and safely prepared by the addition of pyridine to a solution of chromium trioxide in 6 M HCl followed by filtration to obtain the yellow-orange, air-stable solid. The slightly acidic character of the reagent can be modified by buffering the reaction mixture with powdered sodium acetate. By this expedient even such acid-labile groups as tetrahydropyranyl ethers survive. The mildly acidic character of pyridinium chlorochromate has been used to advantage, in essentially a one-flask synthesis of pulegone from citronellol. It has also been used for the conversion of caryophyllene alcohol to caryophyllene ketone[16] (Scheme III.7). Our interest in the chemistry of medium ring compounds[17] prompted us to examine the behaviour of the organoboranes derived from these olefins with pyridinium chlorochromate.

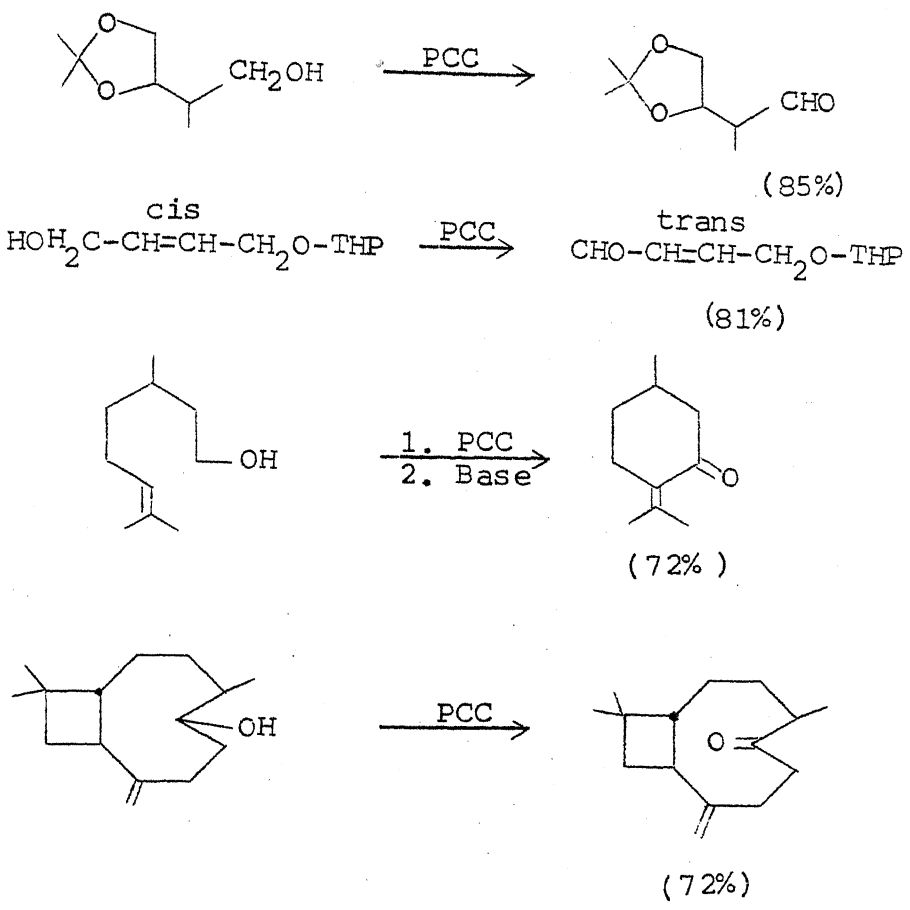
Scheme III.7

$$CH_3-(CH_2)_8-CH_2OH \xrightarrow{PCC} CH_3-(CH_2)_8-CHO \quad (92\%)$$

$$HOH_2C-(CH_2)_4-CH_2OH \xrightarrow{PCC} OHC-(CH_2)_4-CHO \quad (68\%)$$

...contd.

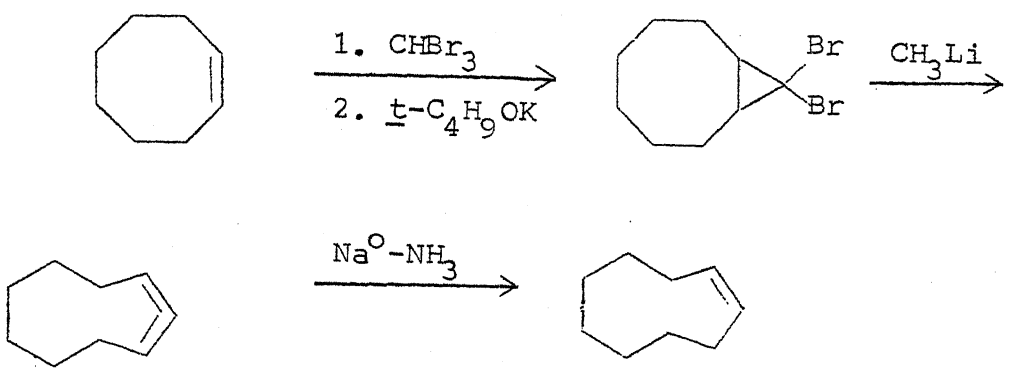
Scheme III.7 (contd.)



III.3 RESULTS AND DISCUSSION

The synthesis of (Z)-cyclononene[18,19] was achieved by a three-step sequence starting from (Z)-cyclooctene as shown in Scheme III.8. Addition of dibromocarbene provided 9,9-dibromobicyclo(6.1.0)nonane in good yield. The identity of this was established by analytical and chemical data. Treatment of gem-bromocompound with methyllithium in ether at -40 to -45° gave 1,2-cyclononadiene in good yield, whose identity was established by elemental analysis and spectral properties. The GLC analysis

Scheme III.8



on a 10 ft 20% Carbowax column indicated it to be 98% pure. Its IR spectrum showed bands at 1950 and 830 cm^{-1} assigned to allenic carbon-carbon double bond stretching and bending frequencies, respectively. Reduction of 1,2-cyclononadiene with sodium in liquid ammonia provided (Z)-cyclononene in 84% yield. The olefin was characterized by elemental analysis, IR and GLC. Similarly (Z)-cyclodecene was synthesized by following the same sequence.

Internal olefins listed in Table III.2 were transformed into the corresponding organoboranes by treatment with BH_3-THF.[20] Tetrahydrofuran was removed under vacuum and the resulting organoborane was dissolved in methylene chloride and treated with excess of pyridinium chlorochromate to obtain the corresponding ketones in 81-92% yield.

Recently, Brown communicated that organoboranes derived from terminal olefins are oxidized by pyridinium chlorochromate to aldehydes in good yield[21] (Scheme III.9). The results are summarized in Table III.3.

Scheme III.9

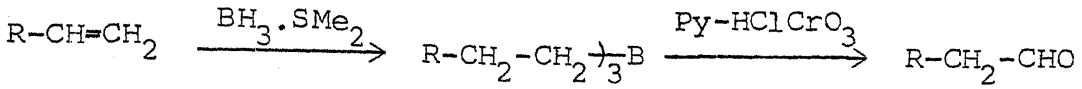


Table III.2

Synthesis of Ketones from Olefins

Alkene	Ketone	Isolated Yield(%)	m.p. of Semicarbazone	
			Found	Lit.
Cyclohexene	Cyclohexanone	81	166°	166°[22]
Cycloheptene	Cycloheptanone	83	163°	163°[23]
(Z)-Cyclooctene	Cyclooctanone	88	167-8°	167-8°[24]
(Z)-Cyclononene	Cyclononanone	92	182-3°	184-5°[25]
(Z)-Cyclodecene	Cyclodecanone	92	203-5°	203-5°[26]
(Z)-Cyclododecene	Cyclododecanone	92	224-5°	226-7°[27]
(E)-4-Octene	Octan-4-one	88	94-5°	95-6°[28]

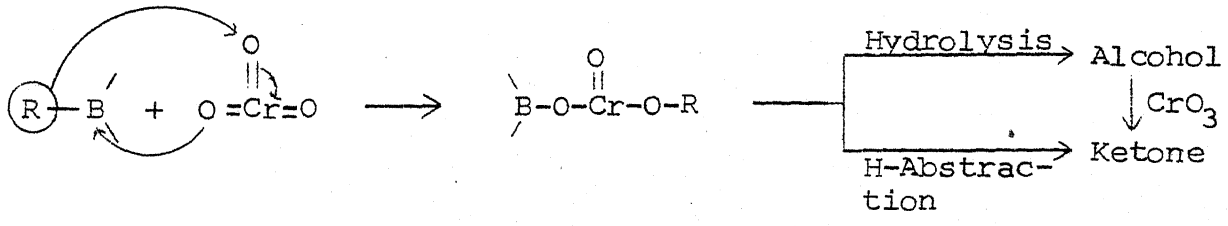
We believe that the oxidation of organoboranes with pyridinium chlorochromate probably proceeds *via* borate esters leading to the formation of alcohols which are subsequently oxidized to ketones. Analysis of an incomplete reaction by IR and GLC showed the presence of alcohol and ketone (Scheme III.10). The fact that the oxidation of organoboranes with pyridinium chlorochromate proceeds *via* the formation of borate esters has been confirmed

Table III.3

Oxidation of Organoboranes from Terminal Olefins with Pyridinium Chlorochromate

Alkene	Product	Product Distribution	Yield (%)
1-Hexene	Hexanal	95	72
	2-Hexanone	5	
1-Octene	Octanal	94	70
	2-Octanone	6	
1-Decene	Decanal	95	74
	2-Decanone	5	
1-Dodecene	Dodecanal	94	78
	2-Dodecanone	6	
3,3-Dimethyl-1-butene	3,3-Dimethylbutanal	98	64
	3,3-Dimethyl-2-butanone	2	

Scheme III.10



by ^{11}B NMR spectrum of aliquots from an incomplete reaction.[29]

The obvious advantages of this method are: (i) the yields are better, (ii) the extraction procedure is easier and employs anhydrous reaction conditions, (iii) this avoids strong acidic medium that is usually employed otherwise. Thus this method is a convenient one step procedure for the oxidation of alkenes to ketones in high yield.

III.4 EXPERIMENTAL

All melting points and boiling points are uncorrected. Melting points were taken on a Fisher-John's melting point apparatus. All IR spectra were recorded on a Perkin-Elmer model 577 as thin film or KBr pellet. GLC analyses were done with Varian Aerograph 90-P Instrument using SE-30,5' or carbowax 15' or 15% carbowax, 5% silvernitrate 10' columns. Microanalyses were carried out by Mr. A.H. Siddiqui of the Department of Chemistry, Indian Institute of Technology, Kanpur, India.

Materials

Bromoform (E. Merck), t-butanol (BDH), tetrahydrofuran (BDH), diglyme (BDH), dichloromethane (HPC), lithium (E. Merck), potassium (E. Merck), sodium (Pfizer), magnesium sulphate (Pfizer), cyclohexene (Koch-light), (Z)-cyclooctene (Cities service), (Z)-cyclododecene (Eastman) were used. All the olefins used under present investigation were distilled over lithium aluminium hydride before use. Ammonia gas supplied in steel tank was distilled directly into the flask.

Preparation of 9,9-Dibromobicyclo(6.1.0)nonane

Potassium t-butoxide was prepared from potassium (20 g, 0.50 g. atom) and dry t-butanol (600 ml). After the removal of excess of t-butanol, dry petroleum ether (500 ml) and (Z)-cyclooctene (55 g, 0.50 mol) were added followed by slow addition of bromoform (126 g, 0.50 mol) at 0°. Usual extraction procedure afforded, 9,9-dibromobicyclo(6.1.0)nonane (100 g, 0.36 mol) in 72% yield, b.p. 85-86°/0.2 mm (lit.[30] b.p. 80-82°/0.1 mm). GLC analysis on a 2 ft silicone rubber column indicated it to be 99% pure.

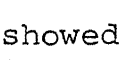
Anal. for $C_9H_{14}Br_2$: Calcd C, 38.30; H, 4.97.
Found C, 38.28; H, 4.93%.

Preparation of 1,2-Cyclononadiene

9,9-Dibromobicyclo(6.1.0)nonane (56.4 g, 0.20 mol) in dry ether (200 ml) was placed in a 500 ml three-necked flask, was swept with a stream of dry nitrogen and cooled to -50 to -60°. Methyllithium prepared from lithium (5.6 g, 0.80 g.atom) and methyliodide (56.8 g, 0.40 mol) was added over a period of one hour. After an additional hour of stirring, the flask was allowed to come to ambient temperature and water was added to destroy excess methyllithium. Usual extraction and work-up procedure gave 1,2-cyclononadiene (20.7 g, 0.17 mol) in 85% yield, b.p. 63°/17 mm (lit.[31] b.p. 62°/16 mm). Its IR spectrum showed bands at 1955 and 845 cm^{-1} characteristic of the allenic function. GLC analysis on a 10' carbowax column indicated it to be 99% pure.

Anal. for C_9H_{14}: Calcd C, 88.51; H, 11.48.
Found C, 88.35; H, 11.44%.

Preparation of (Z)-Cyclononene

A 250 ml three-necked flask was fitted with an inlet tube for ammonia gas, an ethanol liquid nitrogen condenser and a mechanical stirrer. About 150 ml of ammonia was distilled from the tank. Sodium (20.7g, 0.9 g.atom) was added in the form of small pieces and the mixture was stirred for about 15 minutes. 1,2-Cyclononadiene (36.6 g, 0.3 mol) in anhydrous ether (20 ml) was added dropwise with stirring. After stirring for about two hours following the completion of addition, the excess of sodium was decomposed by adding water to the residue remaining after the evaporation of ammonia, was extracted with ether. The combined extracts were washed twice with water and dried over anhydrous magnesium sulphate. Distillation of the residue remaining after the removal of the solvent through an efficient fractionating column gave (Z)-cyclononene (30.5 g, 0.25 mol) in 83% yield, b.p. 81°/40 mm (lit.[32] b.p. 167-69°/740 mm). Its IR spectrum showed an absorption at 710 cm^{-1} (δ ). GLC analysis of the reduction product on a 10' carbowax-silver-nitrate column indicated it to be 99% pure.

Anal. for C_9H_{16}: Calcd C, 87.1; H, 12.9.
Found C, 86.9; H, 12.5%.

Preparation of 10,10-Dibromobicyclo(7.1.0)decane

Following the same procedure as described earlier for the preparation of 9,9-dibromobicyclo(6.1.0)nonane, from (Z)-cyclononene (24.8 g, 0.20 mol), bromoform (50.6 g, 0.20 mol), potassium (8.0 g, 0.20 g.atom) and dry t-butyl alcohol (200 ml), there was obtained 10,10-dibromobicyclo(7.1.0)decane (40.5 g, 0.14 mol) in 68% yield, b.p.80-81°/0.05 mm (lit.[33] b.p. 100°/0.2 mm). The GLC analysis on a 2 ft silicone rubber column indicated it to be 99.5% pure.

Anal. for $C_{10}H_{16}Br_2$: Calcd C, 40.56; H, 5.41.
Found C, 40.49; H, 5.22%.

Preparation of 1,2-Cyclodecadiene

Methyllithium prepared from lithium (2.8 g, 0.4 g.atom) and methyl iodide (28.4 g, 0.20 mol) was treated with 10,10-dibromobicyclo(7.1.0)decane (29.6 g, 0.1 mol) in dry ether between -40 to -45° as already described in the preparation of 1,2-cyclononadiene, there was obtained 1,2-cyclodecadiene (7 g, 0.052 mol) in 52% yield b.p. 60°/4 mm (lit.[34] b.p. 74°/10 mm). The GLC analysis showed it to be 99% pure. Its IR spectrum showed absorptions at 1960 and 865 cm^{-1} characteristic of the allenic group.

Anal. for $C_{10}H_{16}$: Calcd C, 88.23; H, 11.77.
Found C, 88.24; H, 11.79%.

Preparation of (Z)-Cyclodecene

(Z)-Cyclodecene (2.8 g, 0.20 mol) was prepared in 80% yield by sodium-liquid ammonia reduction of 1,2-cyclodecadiene (3.4 g, 0.25 mol) with sodium (2.3g, 0.1 g.atom) in liquid ammonia (100 ml), b.p. 71-72°/12 mm (lit.[35] b.p. 194-195°/740 mm). GLC analysis on 10' carbowax-silvernitrate showed it to be 99% pure. Its IR spectrum showed an absorption at 700 cm^{-1} (δ C=C).

Anal. for $C_{10}H_{18}$: Calcd: C, 86.96; H, 13.04.
Found: C, 86.53; H, 12.87%.

Preparation of Borane in Tetrahydrofuran[20]

A 500 ml three-necked flask fitted with a 250 ml pressure equalizing funnel, was connected through a tygon tubing to a dispersion tube dipped in tetrahydrofuran (250 ml) contained in a 500 ml flask which was cooled externally with freezing mixture. The system was flushed with dry nitrogen. Then the three-necked flask was charged with sodium borohydride (9.5 g, 0.25 mol) in diglyme (125 ml). The pressure equalizing funnel was charged with boron trifluoride etherate (40 ml). Diborane is generated by the dropwise addition of the boron trifluoride etherate over a period of 2-3 hours. After the addition was complete, the reaction flask was heated to 60° for one hour to drive the remaining diborane from diglyme into tetrahydrofuran solution. The sintered glass tube was removed from tetrahydrofuran under a stream of nitrogen and transferred into a bottle. The resulting solution was 1 M in borane (BH_3) as standardized

by measuring the hydrogen evolved on hydrolysis.

Preparation of Pyridinium Chlorochromate[15]

To hydrochloric acid (6 M, 184 ml, 1.1 mol) was added chromium trioxide (100 g, 1 mol) rapidly with stirring. After five minutes the homogeneous solution was cooled to 0° and pyridine (79.1 g, 1 mol)was carefully added over a period of ten minutes to give a yellow-orange solid which was collected on a sintered glass funnel and dried for seven hours in a vacuum desiccator to give pyridinium chlorochromate (181 g, 0.84 mol) in 84% yield. The solid is not appreciably hygroscopic and can be stored for extended periods at room temperature without any change.

Anal. for $C_5H_6NO_3ClCr$: Calcd C, 27.83; H, 2.78; N, 6.50.
Found C, 27.95; H, 2.83; N, 6.31%.

Hydroboration and Pyridinium Chlorochromate Oxidation of Cyclohexene

To a solution of cyclohexene (0.71 g, 9 mmol) in anhydrous tetrahydrofuran (5 ml) was added a solution of borane in tetrahydrofuran (1M, 9 ml, 9 mmol) at 0° under nitrogen atmosphere. The reaction mixture was stirred at 0° for one hour and at room temperature for one hour. Tetrahydrofuran was removed under vacuum and the residual organoborane was dissolved in dichloromethane (20 ml) and cooled to 0° under nitrogen. Pyridinium chlorochromate was then added over a period of 5 minutes and

the reaction mixture was brought to room temperature and stirred for 10 hours. The black reaction mixture was diluted with anhydrous ether (100 ml) and filtered through a pad of anhydrous magnesium sulphate and neutral alumina. The filtrate on evaporation of solvent gave cyclohexanone (0.69 g, 7.0 mmol) in 81% yield. The IR spectrum was identical with that of authentic sample. GLC analysis indicated it to be >99% pure. The m.p. and mixed m.p. of the semicarbazone was 166° (lit.[22] 166°).

Anal. for $C_7H_{13}N_3O$: Calcd C, 54.2; H, 8.39; N, 27.1.
Found C, 54.6; H, 7.90; N, 27.3%.

Hydroboration and Pyridinium Chlorochromate Oxidation of Cycloheptene

Cycloheptene (0.48 g, 5 mmol) was hydroborated using borane-tetrahydrofuran complex (1M, 5 ml, 5 mmol) at 0° and oxidized subsequently using pyridinium chlorochromate (3.24 g, 15 mmol) as described earlier. Cycloheptanone (0.47 g, 4.2 mmol) in 84% was obtained. Its IR spectrum was identical with that of an authentic sample. GLC analysis indicated it to be 99% pure. The m.p. and mixed m.p. of the semicarbazone derivative was 163° (lit.[23] 163°).

Anal. for $C_8H_{15}N_3O$: Calcd C, 56.8; H, 8.88; N, 24.85.
Found C, 57.7; H, 8.51; N, 24.40%.

Hydroboration and Pyridinium Chlorochromate Oxidation of (Z)-Cyclooctene

(Z)-Cyclooctene (0.6 g, 5.5 mmol) was hydroborated using borane-tetrahydrofuran complex (1M, 5.5 ml, 5.5 mmol) and

subsequently oxidized using pyridinium chlorochromate (3.24 g, 15 mmol) as described earlier. Cyclooctanone (0.60 g, 4.8 mmol) was obtained in 88% yield. The IR spectrum was identical with that of an authentic sample. GLC analysis indicated it to be 98% pure. The m.p. and mixed m.p. of the semicarbazone derivative was 167-8° (lit.[24] 167-8°).

Anal. for $C_9H_{17}N_3O$: Calcd C, 59.0; H, 9.29; N, 22.95.
Found C, 59.8; H, 9.50; N, 23.40%.

Hydroboration and Pyridinium Chlorochromate Oxidation of (Z)-Cyclononene

(Z)-Cyclononene (0.63 g, 5 mmol) was hydroborated using borane-tetrahydrofuran (1M, 5 ml, 5 mmol) and subsequently oxidized using pyridinium chlorochromate (3.24 g, 15 mmol) to give cyclononanone (0.66 g, 4.6 mmol) in 92% yield. The IR spectrum was identical with that of an authentic sample. GLC analysis indicated it to be 98% pure. The m.p. and mixed m.p. of the semicarbazone derivative was 183-4° (lit.[25] 184-5°).

Anal. for $C_{10}H_{19}N_3O$: Calcd C, 60.91; H, 9.65; N, 21.35.
Found C, 60.54; H, 9.32; N, 20.85%.

Hydroboration and Pyridinium Chlorochromate Oxidation of (Z)-Cyclodecene

(Z)-Cyclodecene (0.70 g, 5 mmol) was hydroborated using BH_3-THF (1M, 5 ml, 5 mmol) and subsequently oxidized using pyridinium chlorochromate (3.24 g, 5 mmol) as described previously

to give cyclodecanone (0.72 g, 4.7 mmol) in 92% yield. The IR spectrum was identical with that of an authentic sample. GLC analysis indicated it to be 98% pure. M.p. and mixed m.p. of the semicarbazone was 203-5° (lit.[26] 203-5°).

Anal. for $C_{11}H_{21}N_3O$: Calcd C, 62.56; H, 9.95; N, 19.99.
Found C, 62.30; H, 9.51; N, 19.56%.

Hydroboration and Pyridinium Chlorochromate Oxidation of (Z)-Cyclododecene

(Z)-Cyclododecene (0.85 g, 5.1 mmol) was hydroborated using borane-tetrahydrofuran complex (1M, 5.1 ml, 5.1 mmol) and subsequently oxidized using pyridinium chlorochromate (3.3 g, 15.3 mmol) to give cyclododecanone (0.85 g, 4.7 mmol) in 92% yield, m.p. 59-61° (lit.[27] 59-61°). The IR spectrum was identical with that of an authentic sample. GLC analysis indicated it to be 98% pure. M.p. and mixed m.p. of the semicarbazone derivative was 224-5° (lit.[27] 226-7°).

Anal. for $C_{13}H_{25}N_3O$: Calcd C, 65.27; H, 10.46; N, 17.57.
Found C, 64.82; H, 9.96; N, 17.39%.

Hydroboration and Pyridinium Chlorochromate Oxidation of (E)-4-Octene

(E)-4-Octene (0.66 g, 5.9 mmol) was hydroborated using BH_3-THF (1M, 5.9 ml, 5.9 mmol) and subsequently oxidized using pyridinium chlorochomate (3.7 g, 17 mmol) to get 4-octanone

(0.66 g, 5.2 mmol) in 88% yield. Its IR Spectrum was identical with that of an authentic sample. GLC analysis indicate it to be 99% pure. The m.p. and mixed m.p. of the semicarbazone was 94-5° (lit.[28] 95-6°).

Anal. for $C_9H_{19}N_3O$: Calcd C, 58.37; H, 10.27; N, 22.70.
Found C, 58.12; H, 10.14; N, 22.23%.

III.5 REFERENCES

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CHAPTER IV

MONOHYDROBORATION OF ALLENES WITH CATECHOLBORANE[1]

IV.1 ABSTRACT

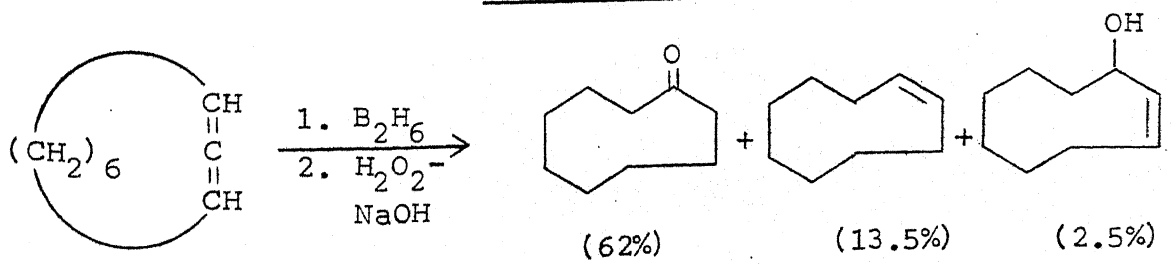
The monohydroboration of 1,2-cyclononadiene, 1,2-cyclodecadiene, 1,2-cyclotridecadiene, 3,4-octadiene and tetramethylallene with catecholborane followed by oxidation resulted in the exclusive formation of the corresponding ketones, due to the regioselective attack of boron at the central carbon atom of the allenic linkage. The monohydroboration of cyclic allenes followed by protonolysis with acetic acid gave the corresponding olefins in excellent yield. The formation of (Z)-cyclononene and (Z)-cyclodecene, indicates the approach of the reagent from hydrogen side and the ring side attack is not possible in the case of 1,2-cyclononadiene and 1,2-cyclodecadiene. In the case of 1,2-cyclotridecadiene the approach of the hydroborating agent is possible from hydrogen side as well as from ring side as evidenced by the formation of (Z)- and (E)-cyclotridecenes (76:24). These results can be explained

in terms of steric and electronic requirements on a four membered transition state.

IV.2 INTRODUCTION

Surprisingly only a few investigations have been done on the hydroboration study of allenes as compared to the isomeric acetylenes. Monohydroboration of allenes with diborane was first reported in 1963.[2] 1,2-Cyclononadiene on monohydroboration-oxidation gave mainly cyclononanone (62%) and small amounts of (Z)-cyclononene (13.5%) and cyclononenol (2.5%). Cyclodecanone (43%), (Z)-cyclodecene (8%) and cyclodecanol (6%) were formed on the monohydroboration of 1,2-cyclodecadiene. However 1,2,6-cyclononatriene reacted only to the extent of 75% and gave 5-cyclononenone (37%) and an unidentified alcohol (2%). Under similar conditions 2,3-nonadiene gave unreacted allene (11%), 3-nonanone (41%) and an unidentified mixture of alcohol (7.2%) and olefin (9%). These results are summarised in Scheme IV.1:

Scheme IV.1



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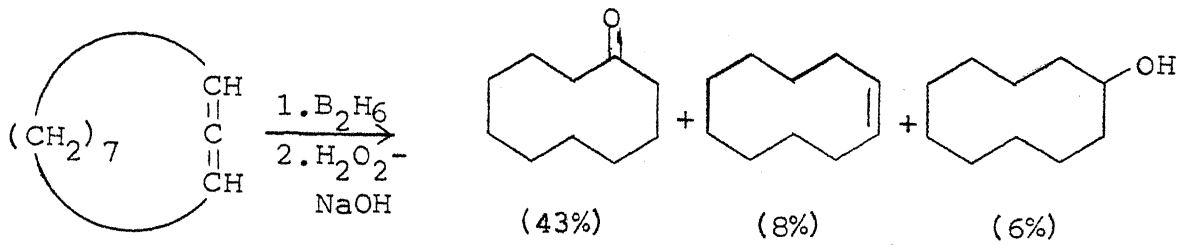
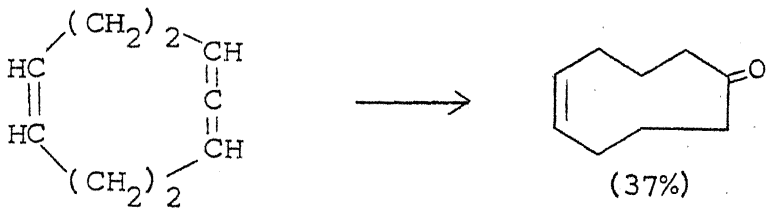
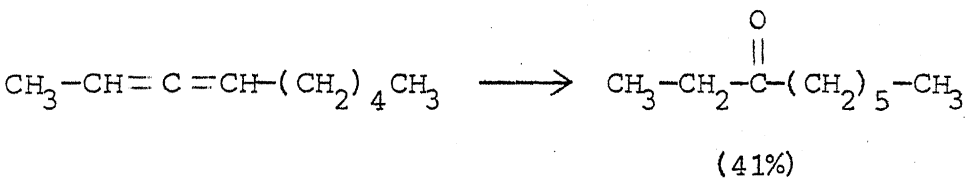
Scheme IV.1 (contd.)

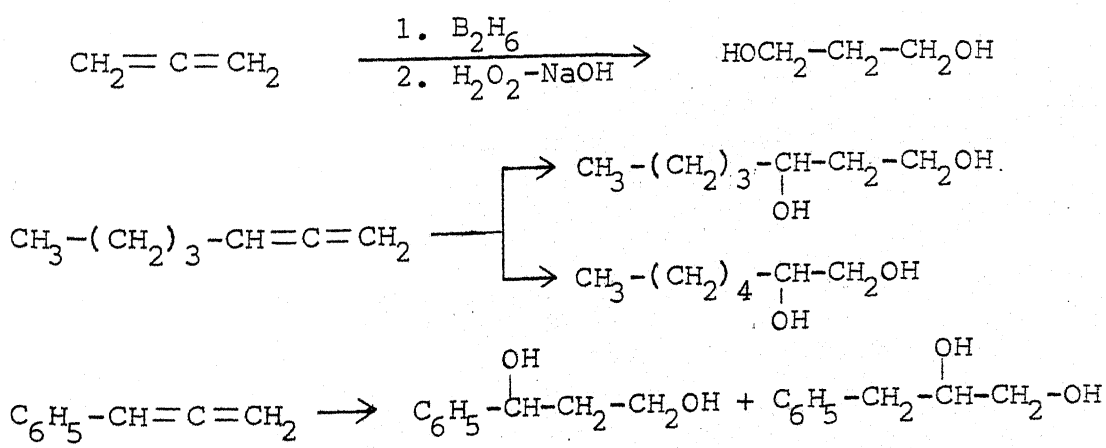






Carsano[3] has reported the dihydroboration of propadiene, 1,2-heptadiene and phenylpropadiene with diborane. Propadiene gave 1,3-propane diol (98%), whereas 1,2-heptadiene and phenylpropadiene yielded a mixture of 1,2- and 1,3-diols after the oxidation of the intermediate organoboranes (Scheme IV.2):

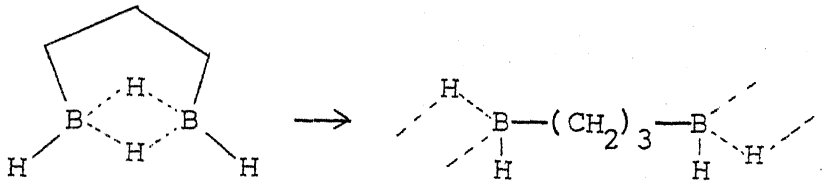
Scheme IV.2



The gas phase reaction of propadiene with excess diborane at 90-95° has been shown to result in the formation of 1,2-trimethylenediborane or its polymer through allyldiborane[4] (Scheme-IV.3):

Scheme IV.3

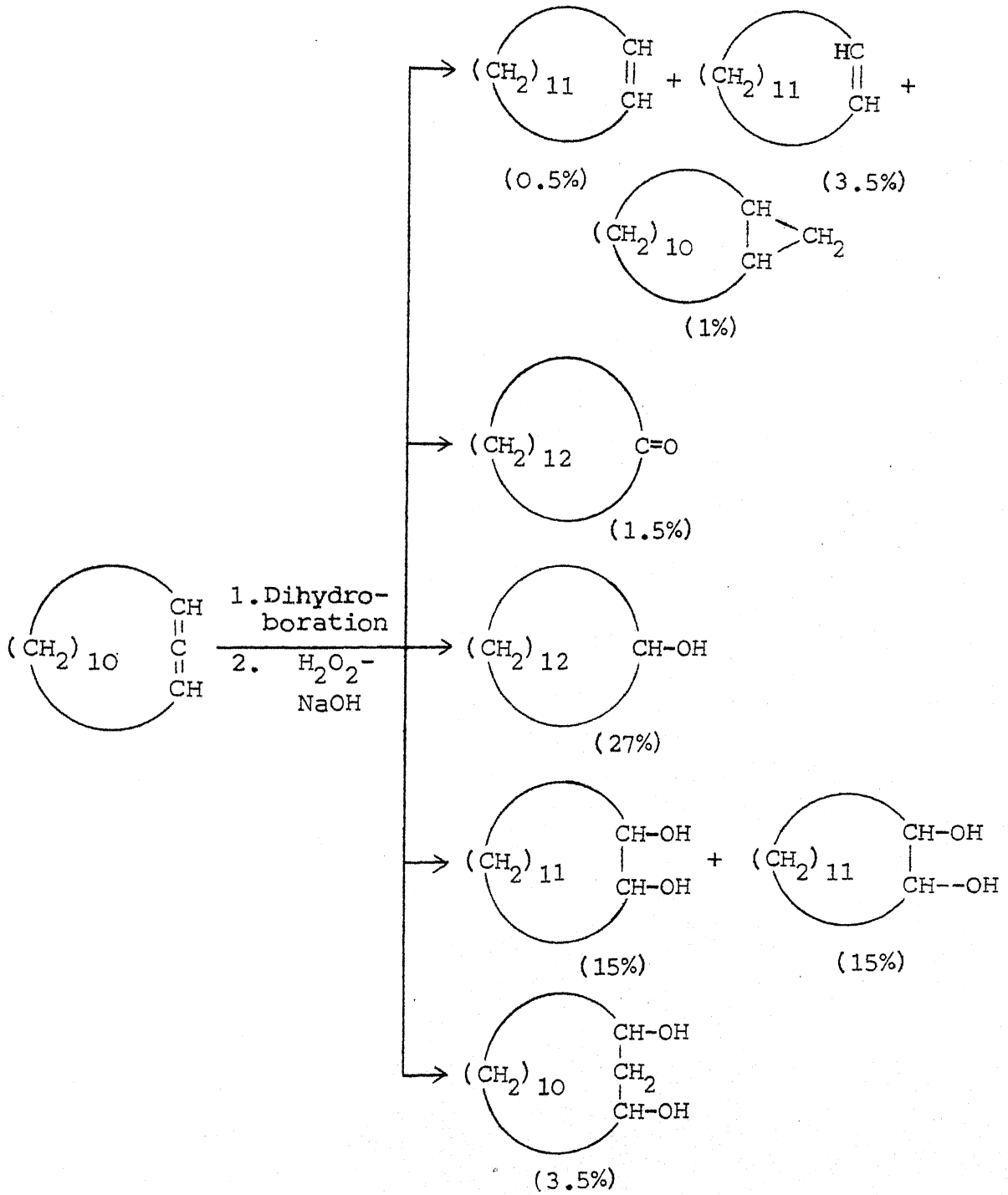
$$CH_2{=}C{=}CH_2 + B_2H_6 \longrightarrow CH_2{=}CH\text{-}CH_2\text{-}B_2H_5$$



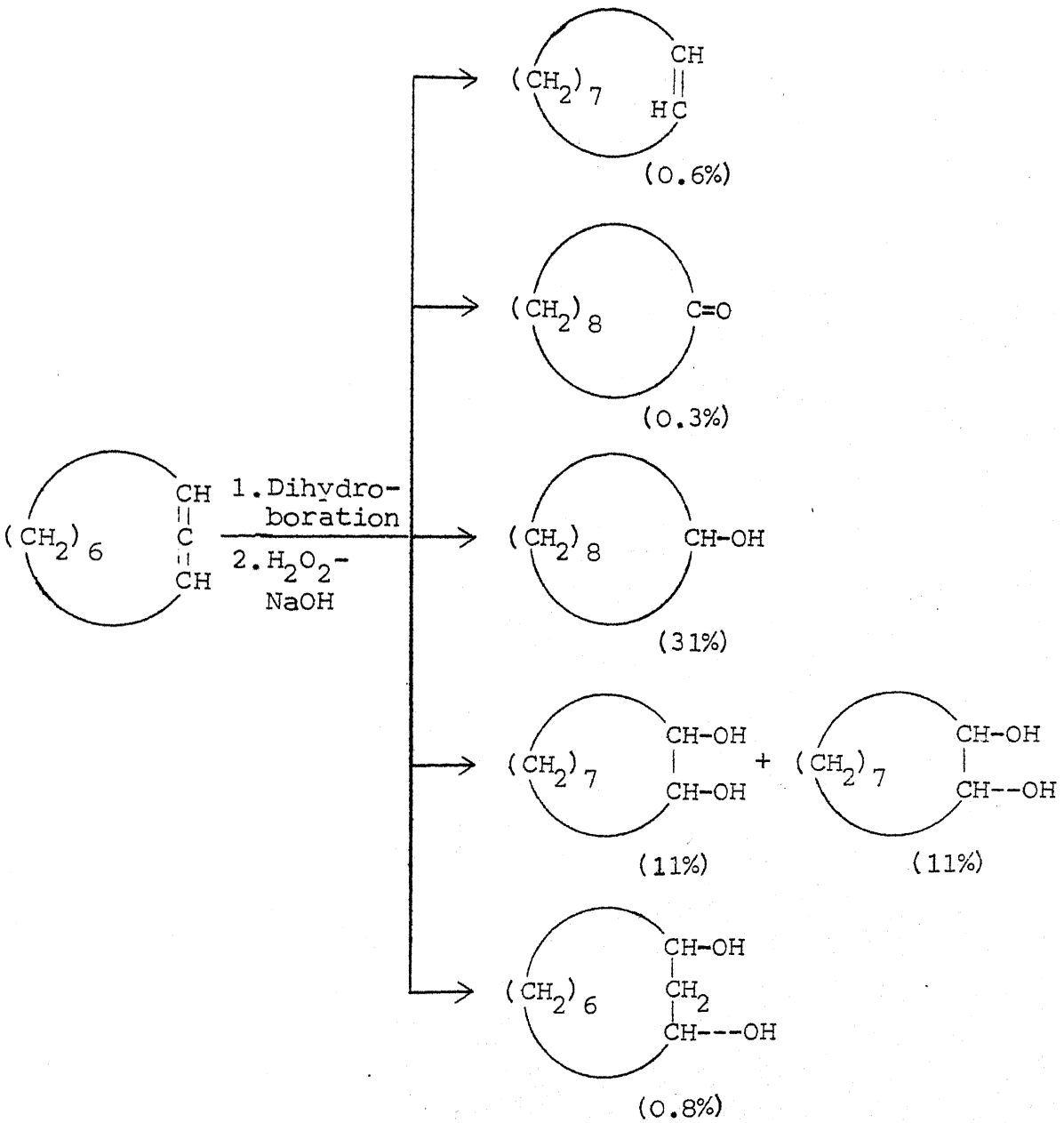
Dihydroboration-oxidation of 1,2-cyclotridecadiene[5-7] gave a mixture of hydrocarbons (5%) containing (Z)-cyclotridecene, (E)-cyclotridecene and bicyclo(10.1.0)tridecane in the ratio 1:7:2, cyclotridecanone (1.5%), cyclotridecanol (27%), (Z)-1,2-cyclotridecane diol (14%), (E)-1,2-cyclotridecane diol (15%) and a mixture of (Z)- and (E)-1,3-cyclotridecane diol (3.5%) (Scheme IV.4). 1,2-cyclononadiene[2,6,7] under similar conditions provided (E)-cyclononene (0.6%), cyclononanone (0.3%), cyclononanol (31%), (Z)-1,2-cyclononane diol (11%), (E)-1,2-cyclononane diol (11%) and (E)-1,3-cyclononane diol (0.8%) (Scheme IV.5). Reasonable mechanistic pathways have been suggested for the formation of these products.[5-8]

Dihydroboration-oxidation of acyclic allenes like 3-ethyl-1,2-pentadiene, 3-phenyl-1,2-butadiene and phenylpropadiene have

Scheme IV.4



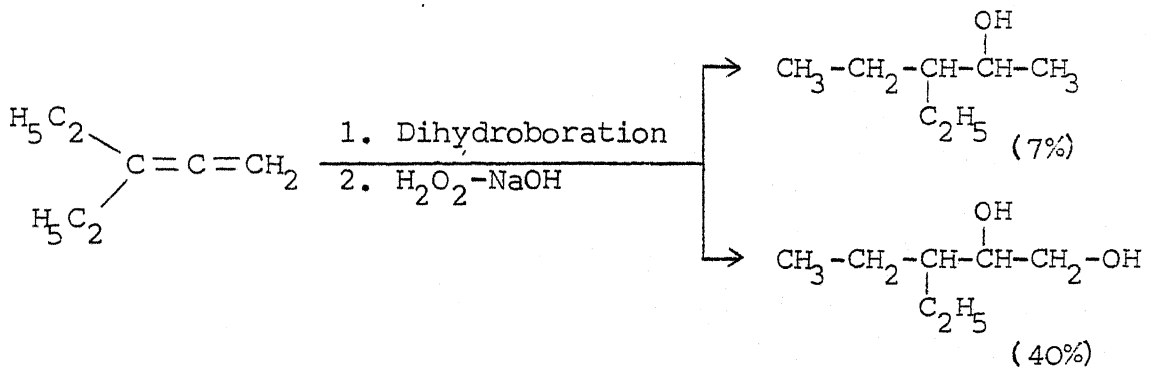
Scheme IV.5

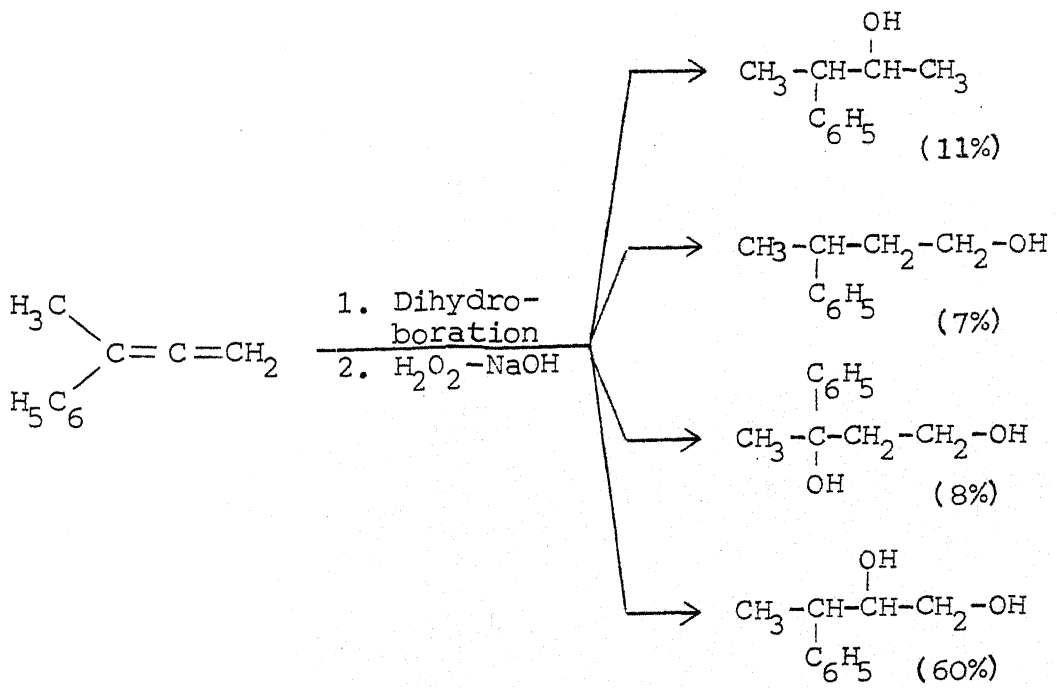


also been studied.[7] 3-Ethyl-2-pentanol (7%) and 3-ethyl-1,2-pentane diol(40%) were obtained by dihydroboration-oxidation of 3-ethyl-1,2-pentadiene. 3-Phenyl-1,2-butadiene under similar

conditions afforded 3-phenyl-2-butanol (11%), 3-phenyl-1-butanol (7%), 3-phenyl-1,3-butanediol (8%) and 3-phenyl-1,2-butanediol (60%). Under the same conditions phenylpropadiene yielded 1-phenyl-1-propanol (2.5%), 1-phenyl-2-propanol (7.5%), 3-phenyl-1-propanol (5%) and 1,3-propanediol (38%). These results are summarised in Scheme IV.6:

Scheme IV.6





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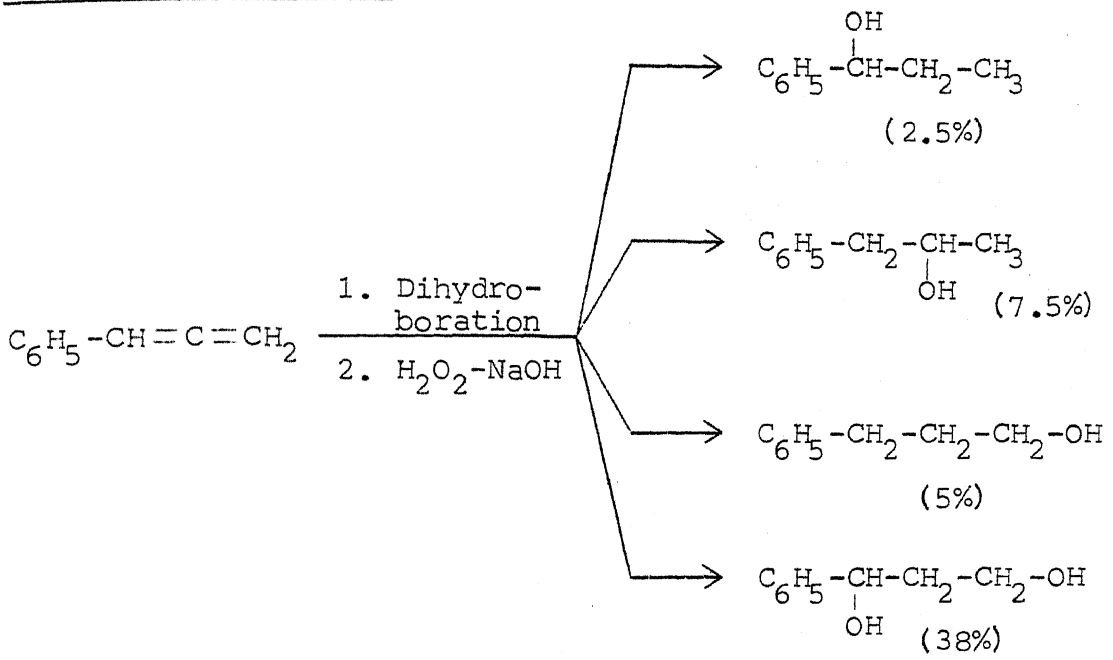
Scheme IV.6 (contd.)



Monohydroboration of 1,2-nonadiene, phenylpropadiene, 3-phenyl-1,2-butadiene, 4,5-nonadiene, tetramethylallene, 1,2-cyclononadiene and 1,2-cyclotridecadiene with disiamylborane followed by oxidation resulted in a mixture of olefins, ketone and alcohol.[9,10] Examination of the products indicated preferential electrophilic attack of boron on the least substituted terminal carbon atom in the case of 1,2-nonadiene, phenylpropadiene, 3-phenyl-1,2-butadiene and on the central carbon atom in 1,2-cyclononadiene, 1,2-cyclotridecadiene, 4,5-nonadiene, in tetramethylallene, boron attack was exclusively on the central carbon atom. The results are summarised in Table IV.1. The formation of various products has been explained in terms of steric effects on a four-centered transition state. The formation of the olefins has been explained by the slow

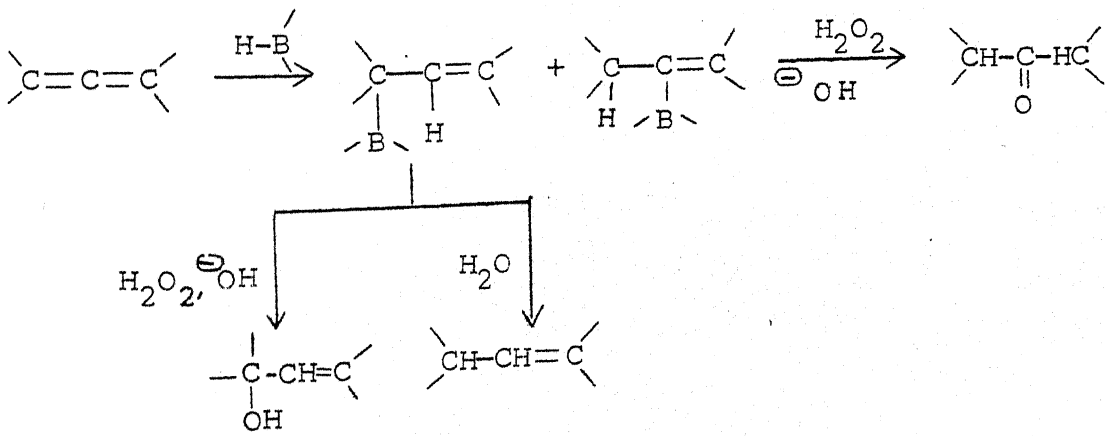
Table IV.1

Percentage of Electrophilic Attack of Boron at the Central and Terminal Carbon Atoms of the Allenic Linkage with Disiamylborane.

Allene	Percentage of Electrophilic Attack of Boron		Percentage Conversion
	Central C atom	Terminal C atom	
1,2-Nonadiene	22	78	100
Phenylpropadiene	20	80	100
3-Phenyl-1,2-butadiene	11.9	88.1	100
4,5-Nonadiene	67.3	32.7	100
Tetramethylallene	100	-	30
1,2-Cyclononadiene	83	17	78
1,2-Cyclotridecadiene	62	38	100

hydrolytic cleavage of the boron-carbon bond of the allylic organoboranes[11] (Scheme IV.7). 1,2-Cyclodecadiene and

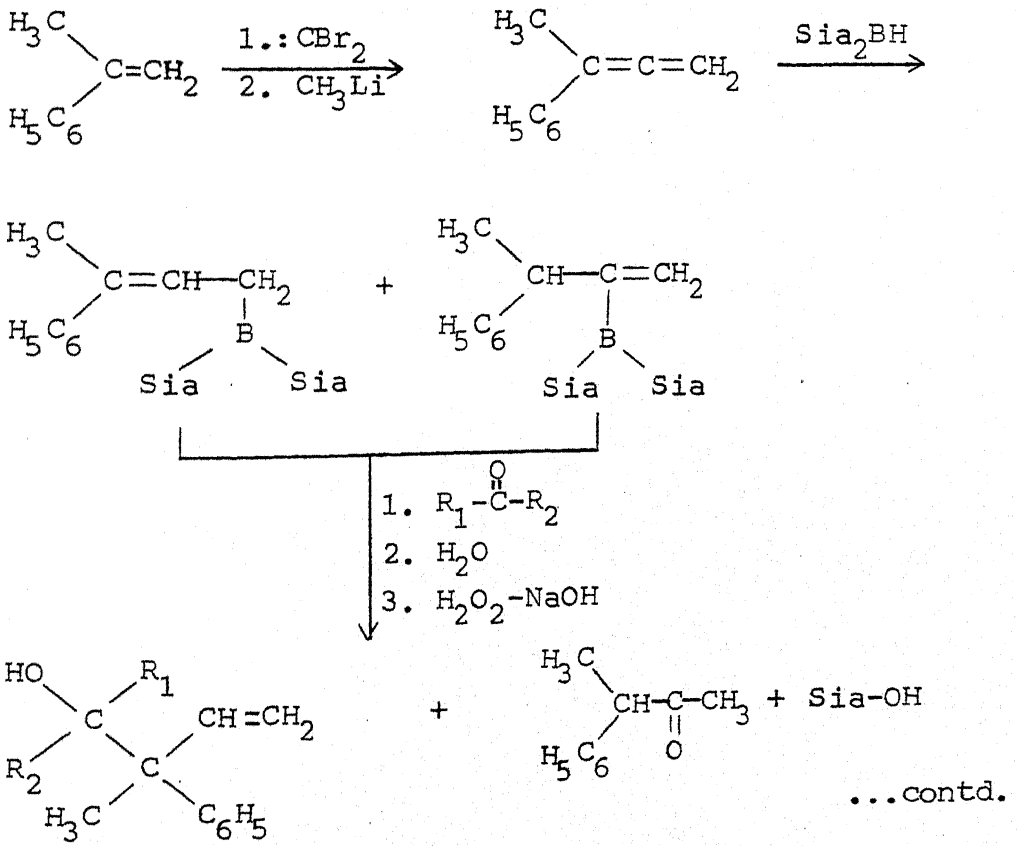
Scheme IV.7



1,2-cyclotridecadiene have undergone monohydroboration with disiamylborane to the extent of 84 and 100% respectively.[12] The protonolysis of the intermediate organoboranes from 1,2-cyclodecadiene yielded 98% pure (Z)-cyclodecene while the intermediate organoboranes from 1,2-cyclotridecadiene yielded 74% of (Z) & 26% of (E)-cyclotridecenes.[12]

A substituted allyl organoborane , disiamyl(3-phenyl-2-butenyl)borane has been prepared *in situ* by the monohydroboration of 3-phenyl-1,2-butadiene with disiamylborane. It reacts readily with butyraldehyde, benzaldehyde, acrolein and acetone to give unsaturated alcohols, possibly *via* a six-membered transition state involving allylic rearrangement[13] (Scheme IV.8):

Scheme IV.8



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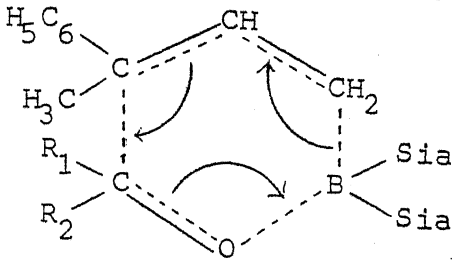
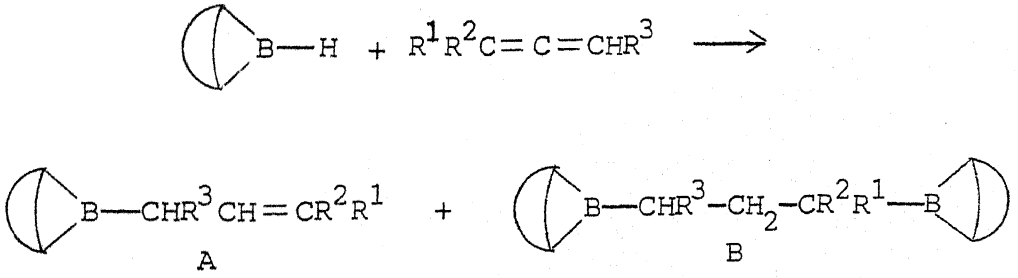
Scheme IV.8 (contd.)



Six-membered transition state

Hydroboration of allenes with 9-borabicyclo[3.3.1]nonane (1:1 mol) gave a mixture of mono- and diaddition products.[14] With the increase of steric hindrance the diaddition decreased (Scheme IV.9). The results obtained with various allenes are summarised in Table IV.2.

Scheme IV.9



The addition of 4,4,6-trimethyl-1,3,2-dioxaborinane (TMDB) to allene, 3-methyl-1,2-butadiene, 2,3-pentadiene, 2,4-dimethyl-2,3-pentadiene and 1,2-cyclononadiene has been studied.[15] The results indicate that attack of the boron atom on the terminal carbon atom of the allenic system is predominant when the terminal carbon atom is unsubstituted. Thus allene (>86%),

Table IV.2

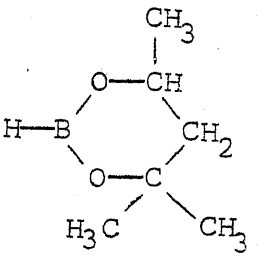
Monohydroboration of Allenes with 9-Borabicyclo[3.3.1]nonane

Allene	Percentage of Allene Reacted	%A	%B
Propadiene	50	0	40
Phenylpropadiene	50	6	43
1,2-Heptadiene	60	25	35
2,3-Pentadiene	80	60	20
3-Methyl-1,2-butadiene	90	85	0

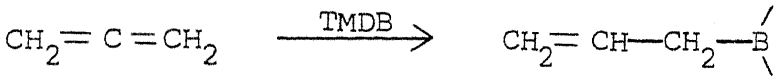
3-methyl-1,2-butadiene (78%) and 2,3-pentadiene (19%) afford decreasing amounts of boron attack at the terminal allenic position. The central carbon atom is preferentially attacked when the allenic system is substituted in the 1 and 3 positions. This is shown in 2,3-pentadiene (81%), 2,4-dimethyl-2,3-pentadiene (100%) and 1,2-cyclononadiene (100%). 3-Methyl-1,2-butadiene, provided 22% attack of boron on the central carbon atom reflecting the effect of methyl substituent on the course of the reaction (Scheme IV.10). The hydroboration reactions were carried out in sealed ampules at 130° for 25-50 hours and the product ratios were determined by GLC. The unusual stability of TMDB and its derivatives has permitted the isolation of intermediate organoboranes and thereby, eliminated the usual oxidation step which Brown and coworkers have employed to detect the point of attack.

Scheme IV.10

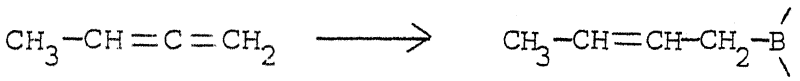
4,4,6-Trimethyl-1,3-dioxa-2-borinane ≡



TMDB

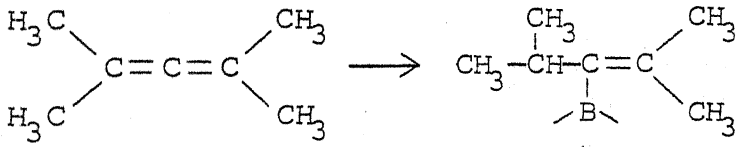


(86%)

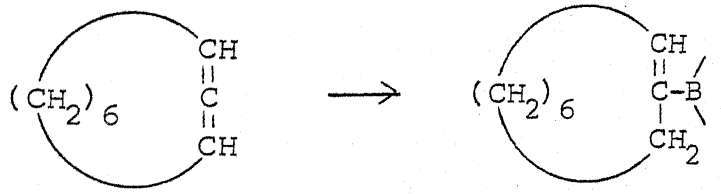


(78 %)

(81%)



(100%)



(100%, cis:trans = 85:15)

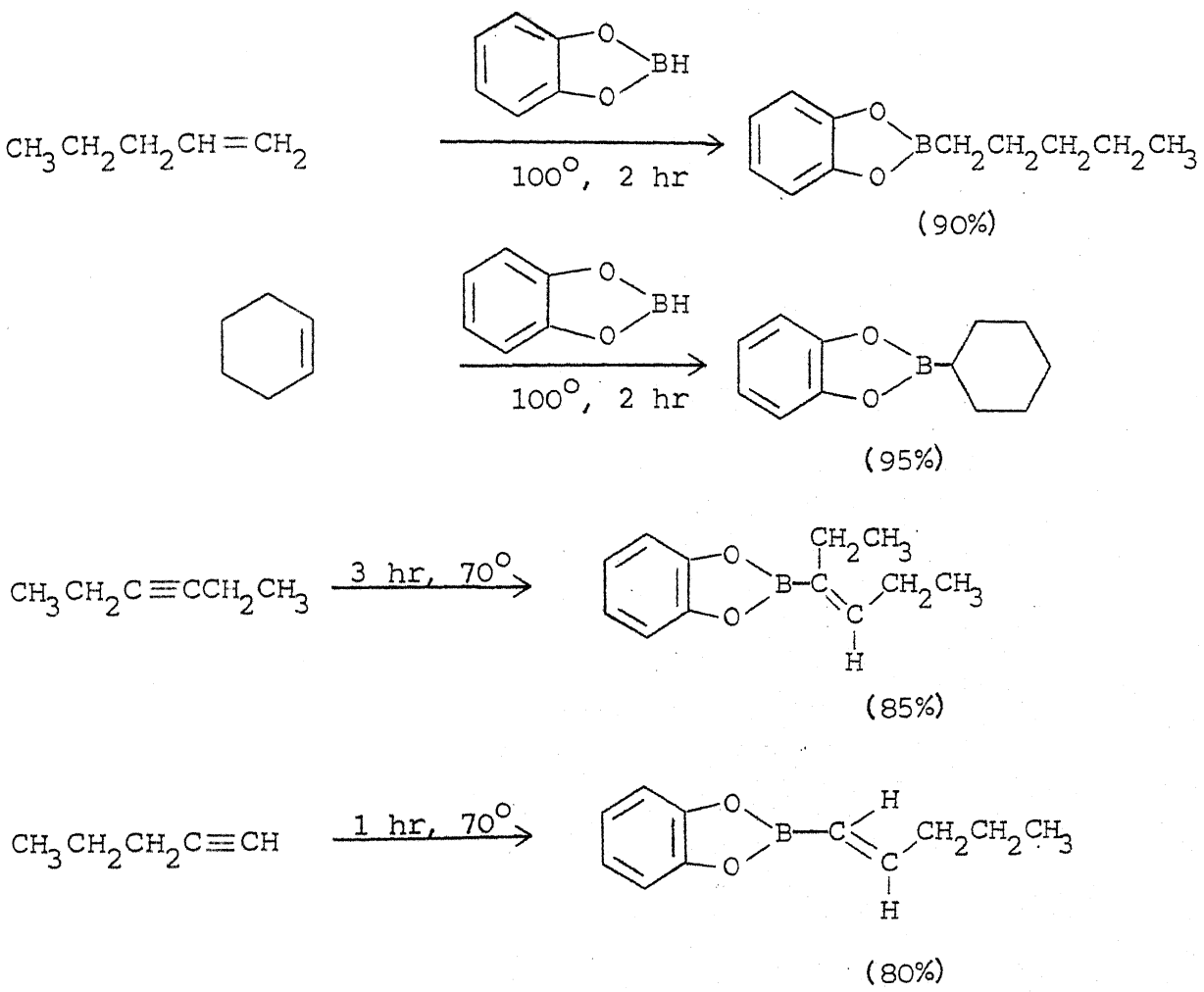
4,4,6-Trimethyl-1,3,2-dioxaborinane is stable[15] but however, 4,4,6-trimethyl-1,3,2-dioxaborinane shows a greatly reduced reactivity to BH_3[16] or to alkylboranes as expected due to π-bonding between boron and oxygen.[17] With catecholborane,

where oxygen is bound to a benzene ring, a dramatic increase is observed in the rate of hydroboration relative to 4,4,6-trimethyl-1,3,2-dioxaborinane. This increased rate of hydroboration is expected since the oxygen 2p electrons can resonate into the benzene ring. Consequently, π-bonding between oxygen and boron is less important. Catecholborane is readily prepared by the reaction of catechol dissolved in tetrahydrofuran with BH_3-THF.[18,19] Catecholborane is remarkably stable when compared to other dialkoxyboranes such as dimethoxyborane[20] and 1,3,2-dioxaborinane[21] which undergo rapid disproportionation. Catecholborane shows no decomposition, by GLC analysis, for upto 4 hours in refluxing tetrahydrofuran or for upto 2 hours at 120° as a neat reagent.[18] Only a 6% loss of hydride activity was observed when a solution of catecholborane in tetrahydrofuran was stirred for 8 hours at 25° in the presence of dry air.

Alkenes and alkynes react very slowly at 25° with catecholborane.[18] But at 100° and 70° the reaction rate is sufficiently rapid for alkenes and alkynes respectively. Internal alkenes required 4 hours at 100° and only 2 hours at 100° in the case of terminal alkenes. Terminal alkynes required 1 hour at 70° while internal alkynes required 2-4 hours at 70° (Scheme IV.11).

Catecholborane is more sensitive to steric effects than BH_3-THF, i.e., a higher percentage of boron substitution is observed at the less hindered carbon atom of the alkene. Catecholborane is less sensitive to the electronic influence of a

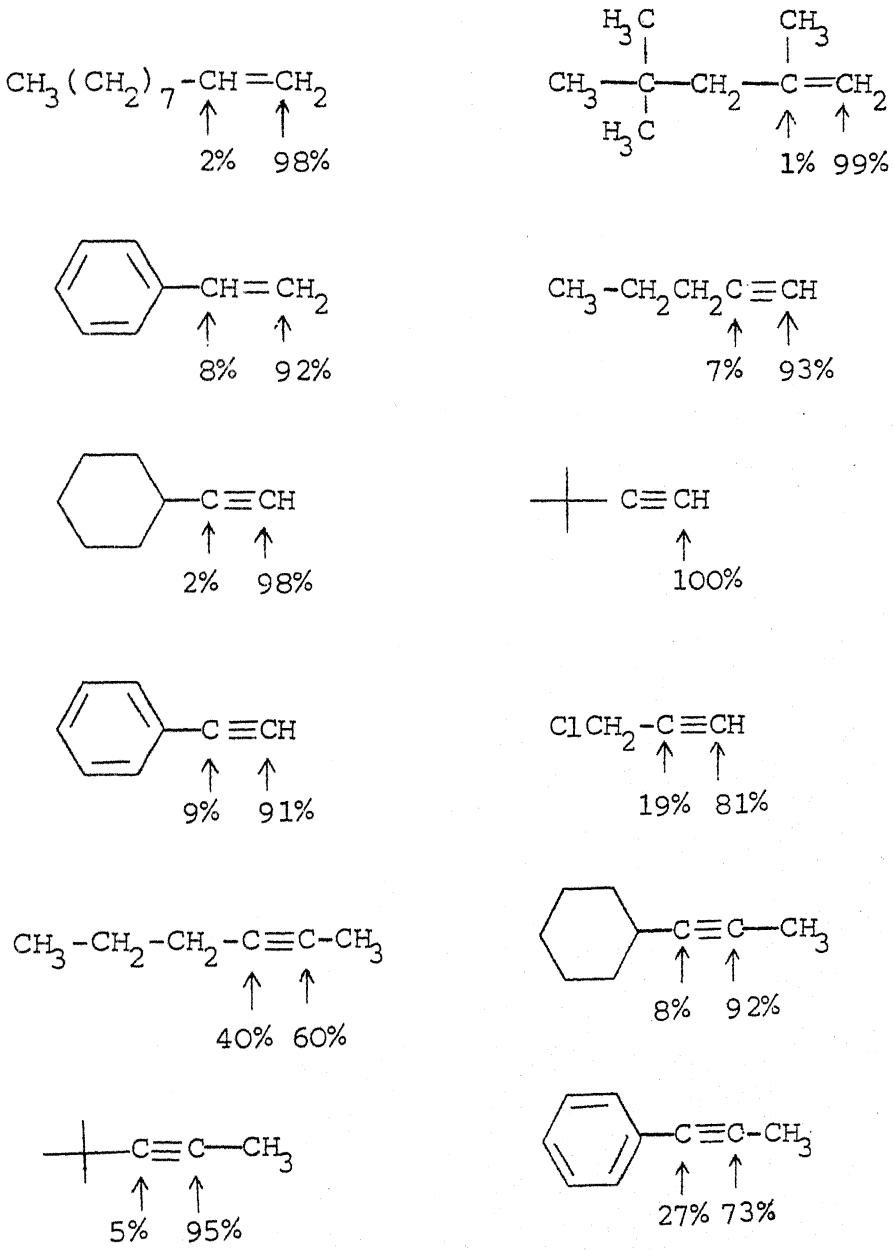
Scheme IV.11



phenyl substituent, i.e., a lower percentage of boron substitution was observed at the benzylic position. The results were illustrated for 1-decene, 2,4,4-trimethyl-1-pentene, styrene, 1-pentyne, cyclohexylethyne, 1-butyne, phenylethyne, 3-chloropropyne, 1-phenylpropyne, cyclohexylpropyne, 2-hexyne and 4,4-dimethyl-2-pentyne in Scheme IV.12.

B-Alkenyl and alkylcatecholboranes were oxidised to alcohols with alkaline hydrogen peroxide, if sufficient sodium

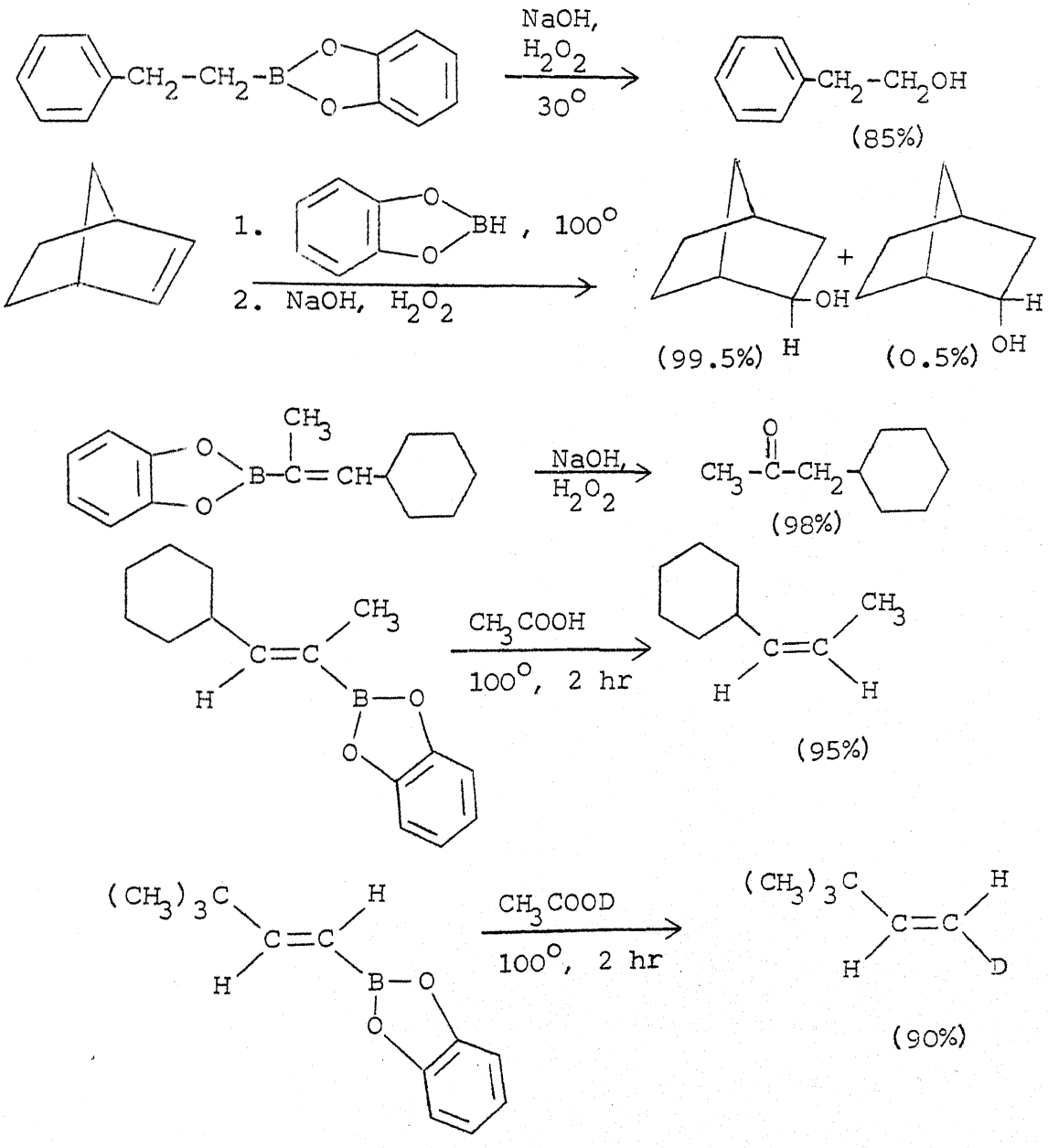
Scheme IV.12



hydroxide was added to react with the liberated catechol to form the corresponding phenolate.[22] Hydroboration of alkenes with catecholborane shows a stereoselectivity comparable to that observed for BH_3-THF. For example, hydroboration-

oxidation of norbornene with catecholborane gives predominantly <u>exo</u> norborneol. Protonolysis and deuterolysis of B-alkenylcatecholboranes proceed readily providing simple, stereospecific syntheses of alkenes (Scheme IV.13):

<u>Scheme IV.13</u>



Thus, the hydroboration of allenes with various hydroborating agents have given various possible products. The aim of the present study was to examine the possibility of stereoselective addition of boron to the allenic linkage with catecholborane,[22] which might offer some useful and interesting synthetic routes. In particular we were interested to study the effect of ring size on the reactivity and selectivity in the direction of addition of catecholborane. Diborane is a multifunctional hydroborating agent and monohydroboration of allenes with diborane might proceed through monoalkyl-, dialkyl- and trialkylborane stages. This means that the steric effect on the transition state for each step in the reaction (Scheme IV.14) may have different steric requirements. Thus, the percentage of

Scheme IV.14

$$R + BH_3 \longrightarrow RBH_2$$

R = Allene.

$$RBH_2 + R \rightarrow R_2BH$$

$$R_2BH + R \rightarrow R_3B$$

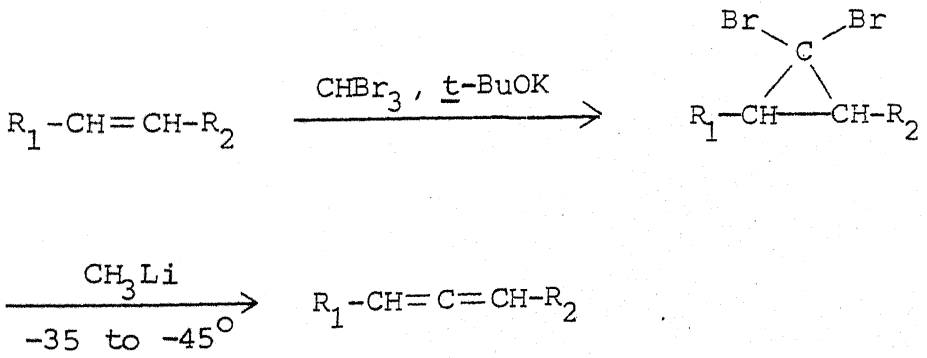
electrophilic attack of diborane at the central and terminal carbon atoms of the allenic linkage will be governed by the cumulative steric effect due to ring size of the allene and the intermediate organoboranes. On the otherhand percentage of electrophilic attack of catecholborane which is a monofunctional reagent, should be controlled only by the steric effect of the

ring size of the allene. The stability of catecholborane even at high temperatures[18] prompted us to examine the hydroboration of 1,2-cyclononadiene, 1,2-cyclodecadiene, 1,2-cyclotridecadiene, 3,4-octadiene, and 2,4-dimethyl-2,3-pentadiene.

IV.3 RESULTS AND DISCUSSION

The syntheses of allenes was achieved by the addition of dibromocarbene to a suitable olefin to obtain 1,1-dibromocyclopropane derivative followed by reaction with methyllithium in ether at -35 to -45°[23] (Scheme IV.15). Catecholborane was prepared by hydroboration of catechol at -5° to -10° under static pressure of dry nitrogen and distilled before use.[18]

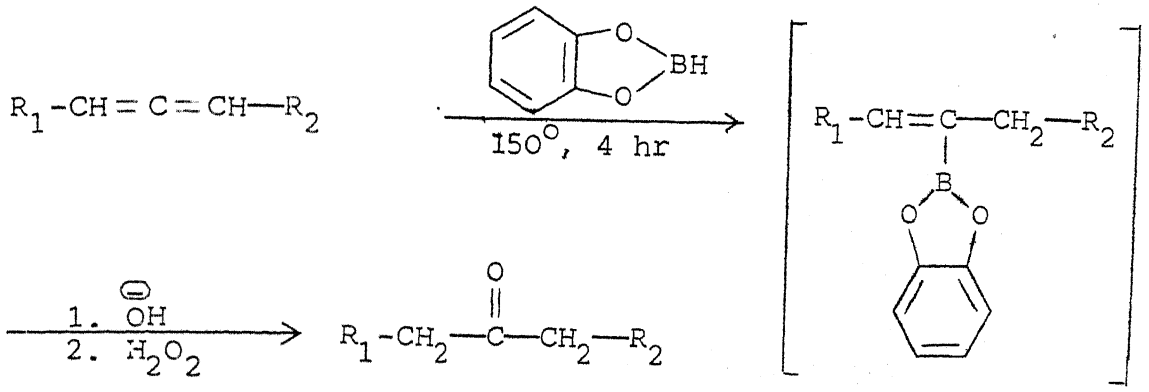
Scheme IV.15



The monohydroboration of allenes was achieved by stirring allene with catecholborane (10% excess) at 150° for 4 hours. The resulting organoborane was oxidized in the usual manner utilizing sodium hydroxide and hydrogen peroxide[18] to give the ketonic

product (Scheme IV.16):

Scheme IV.16



The monohydroboration of 1,2-cyclononadiene with catecholborane followed by oxidation gave cyclononanone (71%) in good yield. The product was readily characterised by its IR which showed strong absorption at 1690 cm^{-1}. The complete absence of absorptions at 1960 and 845 cm^{-1} due to stretching and out-of-plane deformation of allenic linkage clearly shows the absence of starting material. The GLC analysis indicated it to be 99% pure. The results obtained with various allenes are summarised in Table IV.3.

The monohydroboration of cyclic allenes with catecholborane followed by protonolysis with acetic acid in presence of an internal standard gave the corresponding olefins in 96-98% yield (Scheme IV.17). The results obtained with cyclic allenes are summarised in Table IV.4.

Our results on the monohydroboration studies of 1,3-disubstituted allenes with catecholborane clearly demonstrate

Table IV.3

Monohydroboration-Oxidation of Allenes with Catecholborane

Allene	Ketonic Product	Yield (%)	m.p. of Semicarbazone	
			Found	Lit.
1,2-Cyclononadiene	Cyclononanone	71	182-3°	184-5°[24]
1,2-Cyclodecadiene	Cyclodecanone	77	203-5°	203-5°[25]
1,2-Cyclotridecadiene	Cyclotridecanone	73	207-8°	207-8°[26]
3,4-Octadiene	Octan-4-one	61	94-5°	95-6°[27]
2,4-Dimethyl-2,3-pentadiene	2,4-Dimethy-3-pentanone	75	159°	160°[28]

Scheme IV.17

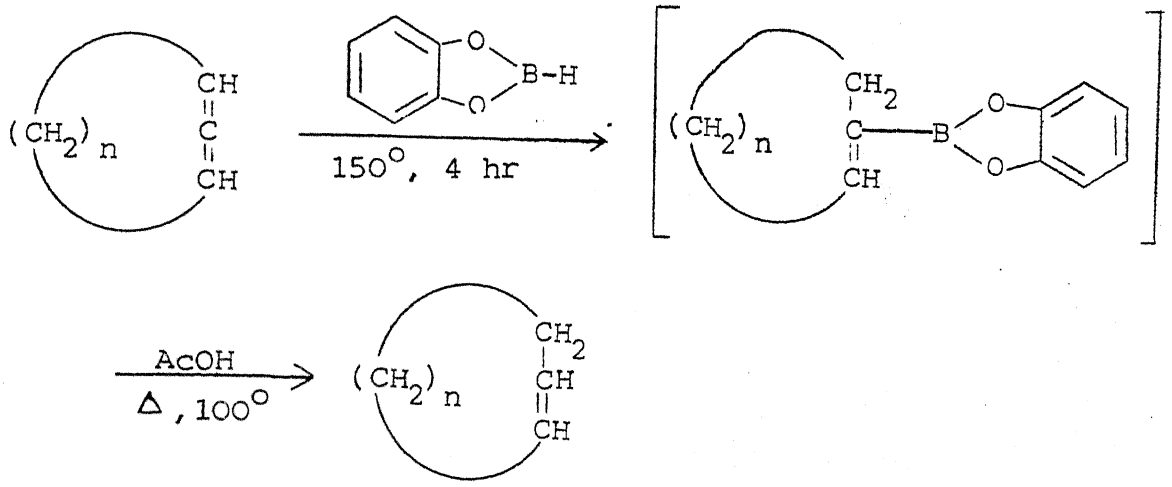


Table IV.4

Monohydroboration-Protonolysis of Cyclic Allenes with Catecholborane

Allene	Olefinic Product	Yield* (%)
1,2-Cyclononadiene	(Z)-Cyclononene	98
1,2-Cyclodecadiene	(Z)-Cyclodecene	96
1,2-Cyclotrideca-diene	(Z)-Cyclotridecene (76%)≠	98
	(E)-Cyclotridecene (24%)≠	

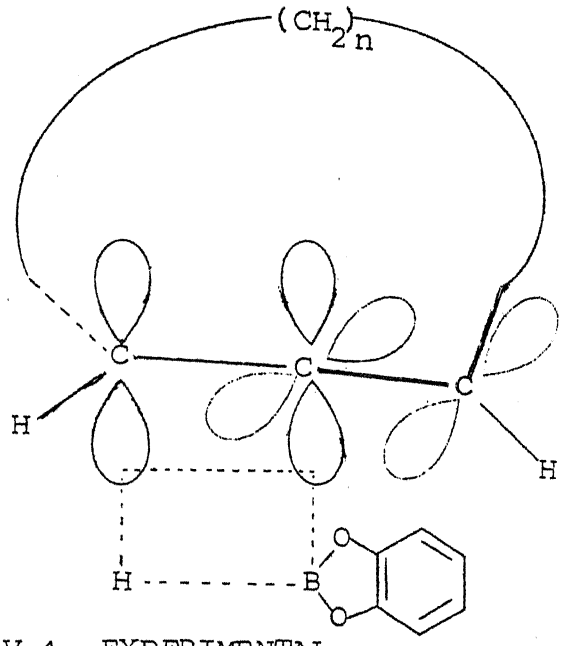
*Calculated by GLC analysis.

≠Separated by preparative GLC.

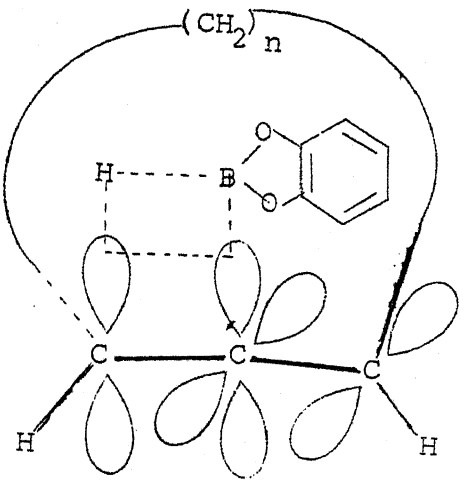
that the attack of boron to allene is regiospecifically at the central carbon atom. Our results with cyclic allenes and tetramethylallene are in complete agreement with the results of Fish[15] who used 4,4,6-trimethyl-1,3-dioxa-2-borinane to hydroborate, 1,2-cyclononadiene and tetramethylallene. However, TMDB has shown only 81% selective attack on the central carbon atom of 2,3-pentadiene. The advantage of this reagent over TMDB is, the reaction times are much less (with TMDB 130°C for 36 hours). In contrast to the reaction with disiamyl borane which results in the formation of olefin by hydrolysis and a mixture of ketone and unsaturated alcohol by oxidation, catecholborane gives exclusively the ketone. Thus the present investigation provides a convenient method for selectively functionalising the central carbon atom of 1,3-disubstituted allenes.

Our results on protonolysis of cyclic allenes can be clearly explained by considering the steric requirements of the hydroborating agent and the conformation of the allene. Hydrogen side attack of the hydroborating agent leads to the formation of (Z)-olefin after protonolysis of the organoborane; ring side attack of the hydroborating agent leads to the formation of (E)-olefin after protonolysis of the intermediate organoborane. Our results on the ratio of (Z:E) cyclotridecenes is in complete agreement with our previous results with disiamyl borane.[12] As there is no unreacted allene present after the reaction, the high yields and high purity (>98%) makes this procedure a convenient route to olefins and ketones from allenes.

HYDROGEN SIDE ATTACK



RING SIDE ATTACK



IV.4 EXPERIMENTAL

All boiling points and melting points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer model-577 Infrared Spectrometer as neat liquids and KBr discs for liquids and solids respectively. Gas-liquid chromatographic analyses were made on Varian Model 90-P Instrument using 15% silicone rubber SE-30; 15% carbowax 20M; 5% $AgNO_3$, 15% carbowax columns (60/80 mesh chromosorb-P was used as the solid support by weight) Microanalyses were performed by Mr. A.H. Siddiqui of the Department of Chemistry, Indian Institute of Technology, Kanpur, India.

Materials

(Z)-Cyclooctene (Cities Service), cyclododecene (Coulumbia), bromoform (SD), methyl iodide (SD), potassium metal (Fischer), sodium borohydride (BDH), lithium (E. Merck), 3-heptene (Aldrich), tetramethylallene(K& K)were used without purification. t-Butanol (BDH) was refluxed over metallic sodium for about 5 hours and

the fraction boiling between 79-81° was collected for the preparation of potassium t-butoxide. Diglyme (Ansul Co.) was kept over calcium hydride and then distilled from lithium aluminium hydride under reduced pressure (b.p. 63-64°/15 mm). Boron trifluoride diethyl etherate (Aldrich) was treated with a small quantity of dry ether (to ensure excess of this component) and distilled under reduced pressure over calcium hydride. Tetrahydrofuran (BDH) was refluxed over sodium wire for six hours and then distilled over lithium aluminium hydride, catechol (E. Merck) was crystallized from toluene and used for the preparation of catecholborane.

General Method of Synthesis of 1,1-Dibromocyclopropane Derivative[23]

In a 1 l. three-necked flask fitted with an efficient mechanical stirrer, a condenser and nitrogen gas inlet and outlet, was placed dry t-butanol (500 ml). Potassium (20.0 g, 0.5 g.atom) was cut into small pieces and added slowly with stirring under nitrogen atmosphere. After all the potassium dissolved at room temperature, the excess t-butanol was removed using a vacuum pump for a period of 2 hours. The solid was crushed into a nice powder and dry petroleum ether 40-60° was added. The flask was cooled to -10° and the olefin (0.5 mol) was added. Bromoform (126 g, 0.5 mol) in petroleum ether (100 ml) was then added dropwise over a period of 6 hours at -10° with stirring. When the addition was over, stirring was continued

for one more hour. Water was added to destroy the unreacted base, and the bromo compound was extracted with petroleum ether (40-60°) and dried over anhydrous magnesium sulphate. The solvent was removed and the product was fractionally distilled under reduced pressure.

Preparation of Methyllithium[29]

A 1 l. two-necked flask fitted with an efficient water condenser, a dropping funnel and nitrogen gas inlet and outlet, was mounted on a magnetic stirrer. Lithium (7.0 g, 1 g.atom) and dry ether (200 ml) were placed in the flask which was swept with dry nitrogen. Methyl iodide (71 g, 0.50 mol) was diluted with dry ether (200 ml) and a few ml was allowed to drop into the flask. As soon as the reaction started (noted by gentle reflux of ether), rest of the methyl iodide solution was added at such a rate that ether refluxed slowly. After the completion of addition, stirring was continued for another hour.

General Method for the Synthesis of Allenes[30]

The 1,1-dibromocyclopropane derivative (0.25 mol) in dry ether (200 ml) was placed in a 1 l. three-necked flask fitted with a dropping funnel and a mechanical stirrer. The flask was swept with a stream of dry nitrogen and cooled to -50 to -60° using ethanol and liquid nitrogen as the coolant. Methyllithium as prepared above was filtered through glass wool in a current of dry nitrogen into a separating funnel and added

dropwise into the flask with stirring over a period of one hour. The flask was allowed to come to ambient temperature and water was added slowly, to destroy excess of methyllithium. The organic compound was extracted with ether, washed several times with water and kept over anhydrous magnesium sulphate. Ether was removed and the allene was distilled under reduced pressure.

Preparation of 9,9-Dibromobicyclo(6.1.0)nonane

Potassium t-butoxide was prepared from potassium (20 g, 0.5 g.atom) and dry t-butanol (600 ml). After the removal of excess of t-butanol, dry petroleum ether (500 ml) and (Z)-cyclooctene (55 g, 0.50 mol) were added followed by slow addition of bromoform (126 g, 0.50 mol) at 0°. Usual extraction procedure afforded 9,9-dibromobicyclo(6.1.0)nonane (100 g, 0.36 mol) in 72% yield, b.p. 85-86°/0.2 mm (lit.[30] b.p. 80-82°/0.1 mm). GLC analysis on a 2 ft silicone rubber column indicated it to be 99% pure.

Anal. for $C_9H_{14}Br_2$: Calcd C, 38.30; H, 4.97.
Found C, 38.38; H, 4.98%.

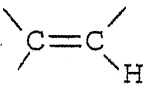
Preparation of 1,2-Cyclononadiene

From 9,9-dibromobicyclo(6.1.0)nonane (56.4 g, 0.20 mol) and methyllithium from lithium (5.6 g, 0.80 g.atom) and methyl iodide (56.8 g, 0.40 mol), 1,2-cyclononadiene (20.7 g, 0.17 mol) was obtained in 85% yield, b.p. 63°/17 mm (lit.[31] b.p. 62/16 mm).

Its IR spectrum showed bands at 1955 and 845 cm^{-1} characteristic of the allenic function. GLC analysis on a 10' carbowax column indicated it to be 99% pure.

Anal. for C_9H_{14}: Calcd C, 88.51; H, 11.48.
Found C, 88.35; H, 11.44%.

Preparation of (Z)-Cyclononene

A 250 ml three necked flask was fitted with an inlet tube for ammonia gas, an ethanol liquid nitrogen condenser and a mechanical stirrer. About 150 ml of ammonia was distilled from the tank. Sodium (20.7 g, 0.9 g.atom) was added in the form of small pieces and the mixture was stirred for 15 minutes. 1,2-Cyclononadiene (36.6 g, 0.3 mol) in anhydrous ether (20 ml) was added dropwise with stirring. After stirring for about 2 hours following the completion of addition, the excess of sodium was decomposed by adding solid ammonium chloride and the residue remaining after the evaporation of ammonia was extracted with ether. The combined extracts were washed twice with water and dried over anhydrous magnesium sulphate. Distillation of the residue remaining after the removal of the solvent through an efficient fractionating column gave (Z)-cyclononene (30.5 g, 0.25 mol) in 83% yield b.p. 81°/40 mm (lit.[31] b.p. 167-168°/740 mm). Its IR spectrum showed an absorption at 710 cm^{-1} (δ ). GLC analysis of the reduction product on a 10' carbowax-silver nitrate column indicated it to be 99% pure.

Anal. for C_9H_{16}: Calcd C, 87.10; H, 12.90.
Found C, 86.93; H, 12.54%.

Preparation of 10,10-Dibromobicyclo(7.1.0)decane

Following the general procedure as described earlier, from (Z)-cyclononene (24.8 g, 0.20 mol), bromoform (50.6 g, 0.20 mol), potassium (8.0 g, 0.20 g.atom) and dry t-butanol (200 ml), there was obtained 10,10-dibromobicyclo(7.1.0)decane (40.5 g, 0.14 mol) in 68% yield, b.p. 80-81°/0.05 mm (lit.[23] b.p. 100°/0.2 mm). The GLC analysis on a 2 ft. silicone rubber column indicated it to be 99.5% pure.

Anal. for $C_{10}H_{16}Br_2$: Calcd C, 40.56; H, 5.41;
Found C, 40.49; H, 5.25%.

Preparation of 1,2-Cyclodecadiene

Methyllithium prepared from lithium (2.8 g, 0.4 g.atom) and methyliodide (28.4 g, 0.20 mol) was treated with 10,10-dibromobicyclo(7.1.0)decane (29.6 g, 0.1 mol) in dry ether between -40 to -45° as already described in the general procedure, there was obtained 1,2-cyclodecadiene (7 g, 0.052 mol) in 52% yield, b.p. 60°/4 mm (lit.[32] b.p.74°/10 mm). The GLC analysis showed it to be $>$ 99% pure. Its IR spectrum showed absorptions at 1960 and 865 cm^{-1} characteristic of the allenic group.

Anal. for $C_{10}H_{16}$: Calcd C, 88.23; H, 11.77.
Found C, 88.25; H, 11.80%.

Preparation of 13,13-Dibromobicyclo(10.1.0)tridecane

From cyclododecene (42 g, 0.25 mol), potassium (10 g, 0.25 g.atom), bromoform (63 g, 0.25 mol) and dry t-butanol (300 ml), there was obtained 13,13-dibromobicyclo(10.1.0)tridecane, b.p. 100-102°/0.02 mm (lit.[33] b.p. 110-115°/0.08 mm). GLC analysis on a 2 ft. silicone rubber column indicated it to be a single compound.

Anal. for $C_{13}H_{22}Br_2$: Calcd C, 46.15; H, 6.51.
Found C, 46.06; H, 6.61%.

Preparation of 1,2-Cyclotridecadiene

13,13-Dibromobicyclo(10.1.0)tridecane (68 g, 0.20 mol) was treated with methyllithium prepared from lithium (5.6 g, 0.80 g-atom) and methyl iodide (56.8 g, 0.4 mol) at -40 to -45° to give 1,2-cyclotridecadiene (28.4 g, 0.16 mol) in 80% yield, b.p.74-76°/0.4 mm (lit.[33] b.p. 83-85°/3 mm). GLC analysis indicated it to be 99% pure.

IR (neat): 1955 and 865 cm^{-1}.

NMR (CCl_4), δ ppm: 1.36 (16H, s), 1.82-2.2 (4H, m), 5.1 (2H, t, J = 4 Hz).

Anal. for $C_{13}H_{22}$: Calcd C, 87.64; H, 12.36.
Found C, 87.62; H, 12.28%.

Preparation of 1,1-Dibromo-2-ethyl-3-propylcyclopropane

From 3-heptene (24.5 g, 0.25 mol), potassium (10 g, 0.25 g.atom), bromoform (63 g, 0.25 mol) and dry t-butanol

(300 ml), there was obtained 1,1-dibromo-2-ethyl-3-propylcyclopropane (35 g, 0.13 mol) in 51% yield, b.p. 38°/0.05 mm. GLC analysis indicated it to be 99% pure.

Anal. for $C_8H_{14}Br_2$: Calcd C, 35.55; H, 5.18.
Found C, 34.53; H, 5.13%.

Preparation of 3,4-Octadiene

1,1-Dibromo-2-ethyl-3-propylcyclopropane (27 g, 0.13 mol) was treated with methyllithium prepared from lithium (5.6 g, 0.80 g.atom) and methyl iodide (56.8 g, 0.40 mol) at -40 to -45° to give 3,4-octadiene (12 g, 0.11 mol) in 86% yield, b.p. 47°/42 mm. IR spectrum showed absorption at 1950 and 850 cm^{-1}. GLC analysis on a carbowax column indicated it to be >98% pure.

Anal. for C_8H_{14}: Calcd C, 87.28; H, 12.73.
Found C, 86.95; H, 12.36%.

Preparation of 1,3,2-Benzodioxaborole[34] (Catecholborane)

A 250 ml three-necked round-bottom flask containing a magnetic stirring bar was fitted with a connecting tube attached to a mercury bubbler, dropping funnel and a stopper. All the glassware was dried in oven for 24 hours at 150° before assembling. The apparatus was cooled to room temperature by flushing dry nitrogen and a static pressure of nitrogen was maintained throughout the experiment. The flask was immersed in an ice bath and borane-tetrahydrofuran (2 M, 55 ml, 0.11 mol) was introduced

into the flask. Pure, thoroughly dry catechol (11 g, 0.1 mmol) was dissolved in tetrahydrofuran (20 ml) and the solution was slowly added to borane over 4 hours. After the addition was complete, the solution was stirred until no more hydrogen was evolved. While passing fast dry nitrogen, a distillation head with a fraction cutter was attached. Tetrahydrofuran was removed under vacuum (40 to 50 mm) at room temperature. After all the tetrahydrofuran has been removed, careful distillation afforded catecholborane (8 g, 0.066 mol) in 66% yield, b.p.76-77°/100 mm (lit.[35] b.p. 88°/156 mm).

Monohydroboration-Oxidation of 1,2-Cyclononadiene with Catecholborane

A mixture of 1,2-cyclononadiene (0.71 g, 5.8 mmol) and catecholborane (0.77 g, 6.4 mmol) was stirred under nitrogen at 150° for 4 hours. It was cooled under dry nitrogen and the organoborane was dissolved in dry tetrahydrofuran (15 ml). Excess hydride was destroyed with 1:10 mixture of water and tetrahydrofuran and cooled to 0°. The oxidation was carried out by dropwise addition of sodium hydroxide (3N, 10.2 ml, 30 mmol) followed by dropwise addition of 30% hydrogen peroxide (4.2 ml, 12 mmol). The temperature was subsequently raised to 25-30°. After 2 hours, the mixture was diluted with water, after saturation with potassium carbonate, the organic compound was extracted with petroleum ether (40-60°). The extract was washed with brine and then dried over anhydrous magnesium sulphate. The solvent

was evaporated after filtration to give cyclononanone (0.57 g, 4.1 mmol) in 71% yield, b.p. 90-91°/10 mm (lit.[24] b.p. 94-95°/13 mm). It was 98% pure as analyzed by GLC on carbowax and SE-30 columns. Its IR was identical with that of an authentic sample. The semicarbozone of cyclononanone had m.p. and mixed m.p. 184-185° (lit.[24] 184-185°).

Anal. for $C_{10}H_{19}N_3O$: Calcd C, 60.91; H, 9.65; N, 21.35.
Found C, 59.98; H, 9.23; N, 20.82%.

Monohydroboration-Oxidation of 1,2-Cyclodecadiene with Catecholborane

A mixture of 1,2-cyclodecadiene (0.70 g, 5.2 mmol) and catecholborane (0.70 g, 5.8 mmol) was stirred under nitrogen at 150° for 4 hours. By following the same work-up procedure as described earlier, cyclodecanone (0.61 g, 4 mmol) was obtained in 77% yield, b.p. 84°/4 mm (lit.[25] b.p. 100-102°/12 mm). Its identity was readily established by comparison of GLC retention times and IR with that of an authentic sample. M.p. and mixed m.p. of the semicarbazone was 203-205° (lit.[25] 203-205°).

Anal. for $C_{11}H_{21}N_3O$: Calcd C, 62.56; H, 9.95; N, 19.99.
Found C, 62.35; H, 9.54; N, 19.58%.

Monohydroboration-Oxidation of 1,2-Cyclotridecadiene with Catecholborane

A mixture of 1,2-cyclotridecadiene (0.87 g, 4.9 mmol) and catecholborane (0.66 g, 5.5 mmol) was stirred under nitrogen

at 150° for 4 hours. By following the same work-up procedure as described earlier, cyclotridecanone (0.70 g, 3.6 mmol) was obtained in 73% yield, b.p. 87-88°/ 1 mm (lit.[26] 138°/12 mm). Its identity was readily established by GLC retention times and IR spectra with that of an authentic sample. Its semicarbazone had a m.p. and mixed m.p. 207-208° (lit.[26] 207-208°).

Anal. for $C_{14}H_{27}N_3O$: Calcd C, 66.40; H, 10.68; N, 16.60.
Found C, 65.98; H, 10.23; N, 16.63%.

Monohydroboration-Oxidation of 3,4-Octadiene with Catecholborane

A mixture of 3,4-octadiene (1.1 g, 10 mmol) and catecholborane (1.3 g, 11 mmol) was stirred under nitrogen atmosphere at 150° for 4 hours. By following the same work-up procedure as described earlier yielded,octan-4-one (0.78 g, 0.61 mol) in 61% yield, b.p. 66°/20 mm (lit.[27] b.p. 70°/26 mm). Its identity was readily established by comparison of GLC retention times and IR with that of an authentic sample. Its semicarbazone had a m.p. and mixed m.p. 94-95° (lit.[27] 95-96°).

Anal. for $C_9H_{19}N_3O$: Calcd C, 58.37; H, 10.27; N, 22.70.
Found C, 58.12; H, 10.14; N, 22.23%.

Monohydroboration-Oxidation of 2,4-Dimethyl-2,3-pentadiene

A mixture of 2,4-dimethyl-2,3-pentadiene (0.96 g, 10 mmol) and catecholborane (1.3 g, 11 mmol) was stirred under nitrogen

atmosphere at 150° for 4 hours. By following the same work-up procedure as described earlier, 2,4-dimethyl-3-pentanone (0.90 g, 0.79 mol) was obtained in 79% yield, b.p. 60°/40 mm (lit.[36] b.p. 123-126°). Its identity was readily established by GLC retention times and IR spectra with that of an authentic sample. Its semicarbazone m.p. and mixed m.p. is 160° (lit.[28] 160°).

Anal. for $C_8H_{17}N_3O$: Calcd C, 56.14; H, 9.94; N, 24.56.
Found C, 56.93; H, 9.37; N, 24.43%.

Hydroboration-Protonolysis of 1,2-Cyclononadiene with Catecholborane

A mixture of 1,2-cyclononadiene (0.35 g, 2.9 mmol) and catecholborane (0.40 g, 3.3 mmol) was stirred under nitrogen atmosphere at 150° for 4 hours. It was cooled under nitrogen atmosphere. Excess hydride was destroyed with a few drops of ethylene glycol. Glacial acetic acid (5 ml) and internal standard n-decane were added to the reaction mixture and stirred at 100° for 4 hours, extracted with petroleum ether (40-60°), washed with ice cold sodium hydroxide (1 N) and then with distilled water till neutral, dried over anhydrous magnesium sulphate and filtered through a bed of silica-gel to get (Z)-cyclononene in 98% yield (by GLC analysis). The product was identified by superimposable IR with that of authentic sample.

Hydroboration-Protonolysis of 1,2-Cyclodecadiene with Catecholborane

A mixture of 1,2-cyclodecadiene (0.29 g, 2.1 mmol) and catecholborane (0.30 g, 2.5 mmol) was stirred under nitrogen

atmosphere at 150° for 4 hours. It was cooled under nitrogen and excess of hydride was destroyed with ethylene glycol and glacial acetic acid (5 ml) was added alongwith internal standard n-decane and stirred at 100° for 11 hours and worked up as described above to get (Z)-cyclodecene in 96% yield. The product was readily identified by superimposable IR with that of an authentic sample.

Hydroboration-Protonolysis of 1,2-Cyclotridecadiene with Catecholborane

A mixture of 1,2-cyclotridecadiene (0.465 g, 2.6 mmol) and catecholborane (0.36 g, 3 mmol) was stirred under nitrogen atmosphere at 150° for 4 hours. It was cooled under dry nitrogen and excess of hydride was destroyed with ethylene glycol. Glacial acetic acid (5 ml) was added along with the internal standard n-dodecane and stirred at 100° for 2 hours and worked up as described above to get a mixture of (Z)-cyclotridecene and (E)-cyclotridecene in the ratio of 74:26 respectively. The two components were separated by preparative GLC on a 15' carbowax column and readily identified by superimposable IR with those of authentic samples.

IV.5 REFERENCES

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CHAPTER V

COUPLING REACTIONS OF VINYLBORONICACIDS

V.1 ABSTRACT

Alkyl substituted vinylboronicacid like trans-β-n-heptylethenylboronic acid with silver nitrate in presence of a base gave 1-nonene in 71% yield and the desired (E, E)-8, 10-octadecadiene in 24% yield. But trans-β-phenylethenylboronic-acid on similar reaction gave only styrene as the exclusive product. However, reaction of trans-β-phenylethyenylboronic acid with bis(benzonitrile)palladium(II) chloride in presence of base gave the desired (E, E)-1, 4-diphenyl-1, 3-butadiene in excellent yield. On the other hand trans-β-n-heptylethenylboronicacid gave 1-nonene 14% and a mixture of (Z, Z), (Z, E), (E, E)-8, 10-octadecadienes in 76% yield in the ratio of 3:30:67. trans-β-p-Tolylethenylboronicacid and trans-β-p-methoxyphenyl-ethenylboronicacid on similar treatment gave the desired (E, E)-1, 4-bis(p-methylphenyl)-1, 3-butadiene and (E, E)-1, 4-bis-(p-methoxyphenyl)-1, 3-butadiene respectively in excellent yield.

We suggest that the reaction proceeds through dichlorodivinyl-palladiumdianion to form the corresponding vinyl radicals which in turn lead to the formation of the various products. Thus the present investigation provides an excellent method for the syntheses of (E,E)-1,4-diaryl-1,3-butadienes from arylacetylenes.

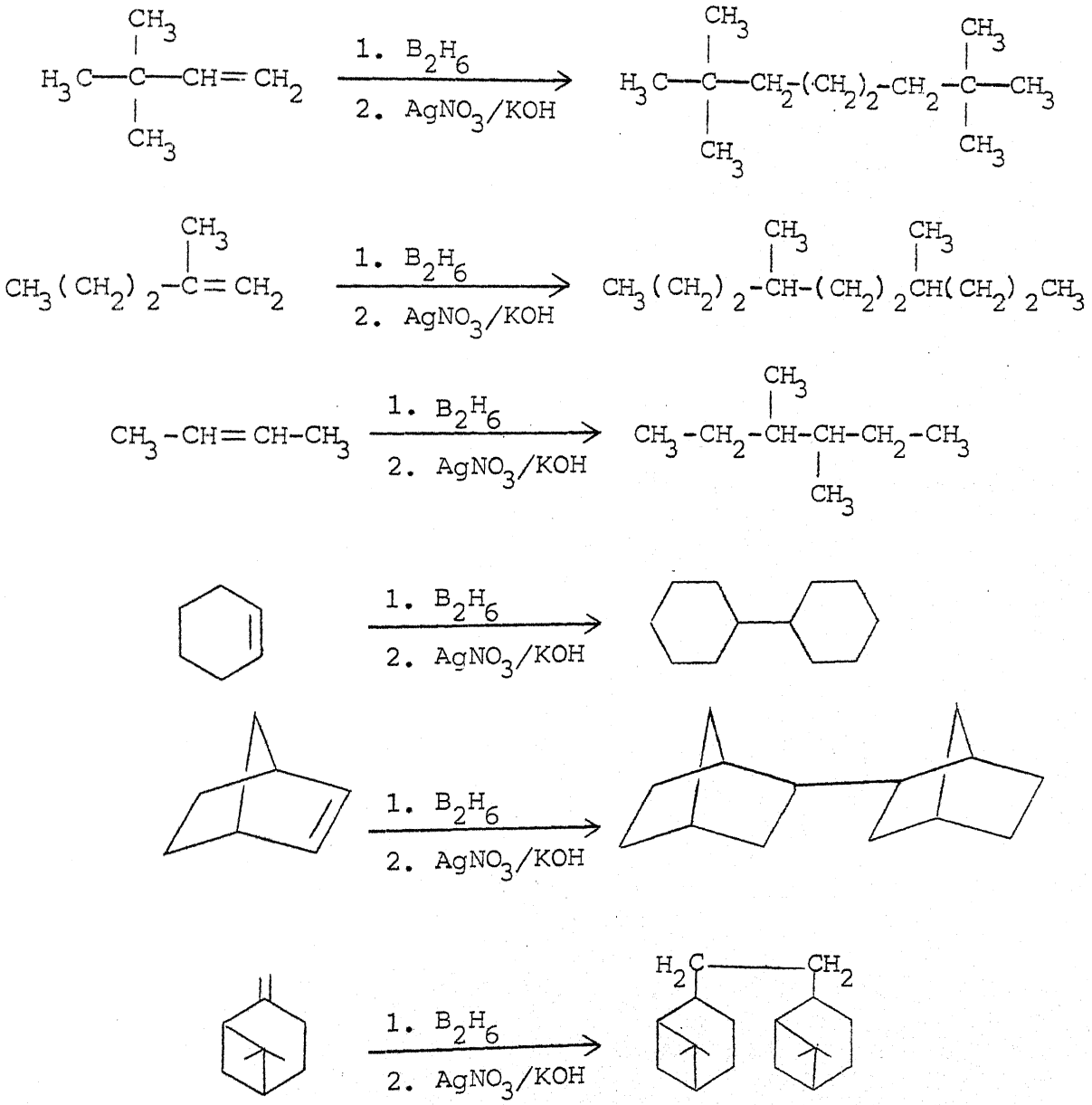
V.2 INTRODUCTION

The building up of a desired carbon structure through carbon-carbon linkage can be achieved *via* organometallics.[1] Accordingly, the possibility of using organoboranes for this purpose has been explored to a limited extent. Silver salts have been found to be quite effective in bringing about the coupling of the alkyl groups of organometallics.[2] Johnson and coworkers[3,4] for the first time carried out the reaction of organoborane, such as *n*-hexylboronic acid with ammoniacal silver nitrate and reported the coupling of alkyl moieties in low yield. Later Brown and coworkers[5] demonstrated a remarkable effect in the yield of the coupling product when trialkylboranes were treated with silver nitrate in alkaline medium. The method has been developed to achieve the coupling of a variety of alkyl groups in high yields directly in the hydroboration flask by mere treatment of the trialkylborane with silver nitrate and potassium hydroxide (Scheme V.1).[5,6]

The reaction has also been extended to couple, two different alkyl groups, and to substrates containing functional

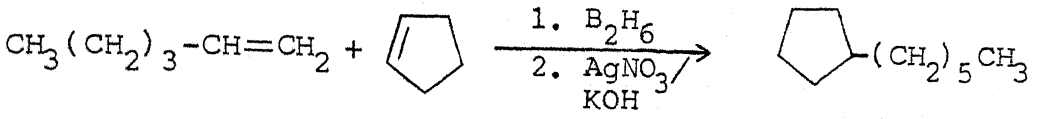
groups that are not affected during hydroboration reaction (Scheme V.2).[5,6]

Scheme V.1



Scheme V.2

$$CH_3(CH_2)_3-CH=CH_2 + CH_3(CH_2)_2-CH=CH_2 \xrightarrow[2.\ AgNO_3/KOH]{1.\ B_2H_6} CH_3-(CH_2)_9-CH_3$$



$$CH_3(CH_2)_3-CH=CH_2 + \xrightarrow[2.\ AgNO_3/KOH]{1.\ B_2H_6}$$

$$CH_3-C(CH_3)=CH_2 + CH_2=CH(CH_2)_8CO_2C_2H_5 \xrightarrow[2.\ AgNO_3/KOH]{1.\ B_2H_6} CH_3-CH(CH_3)-(CH_2)_{11}-CO_2C_2H_5$$

The observed coupling reaction was explained by a radical intermediate, formed through alkyl silver intermediate (Scheme V.3):

Scheme V.3

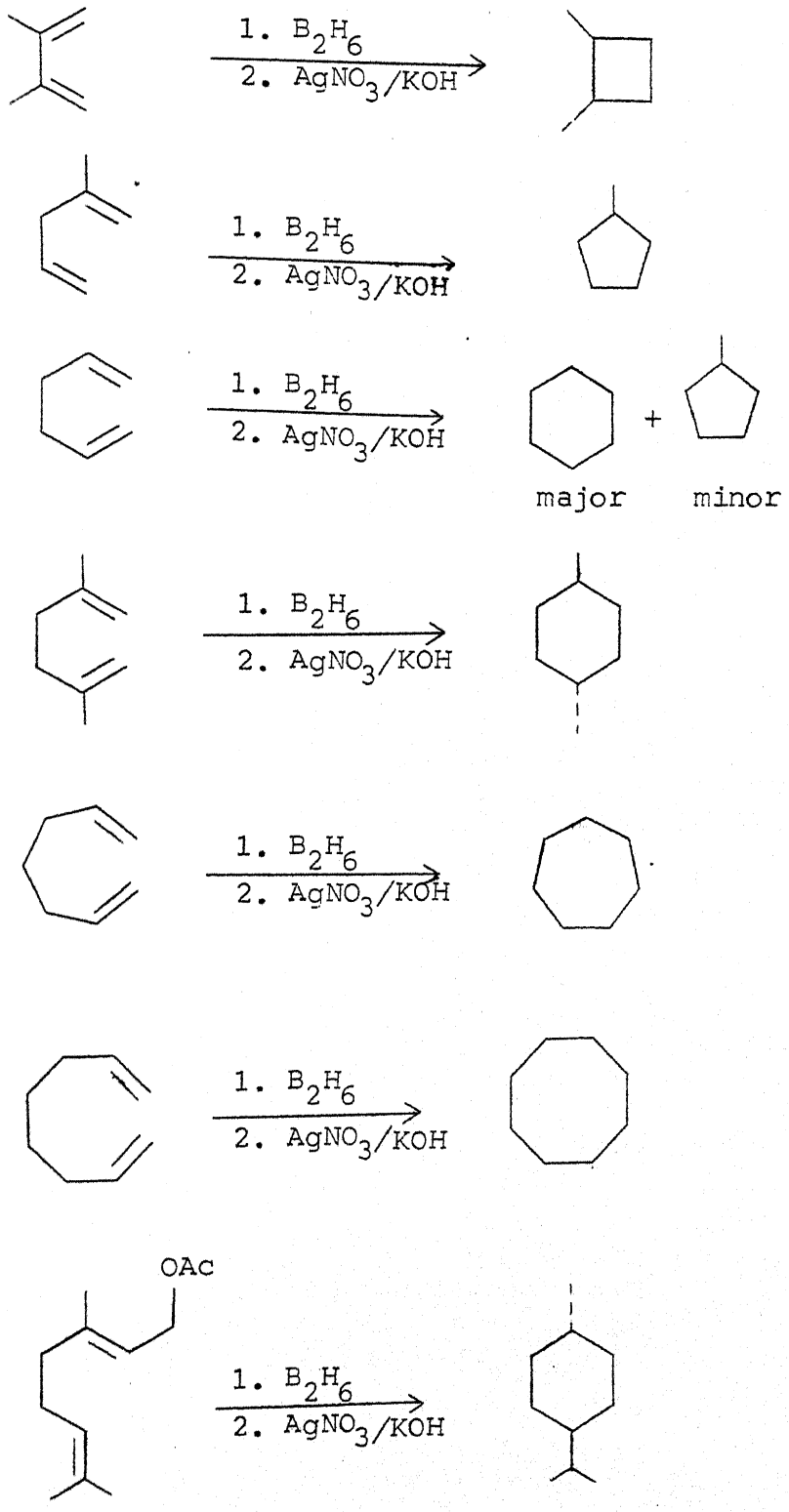
$$\text{B}(\text{—R})_2 + AgOH \longrightarrow R-Ag + \text{B}(\text{—OH})_2$$

$$R-Ag \longrightarrow R\cdot + Ag\cdot$$

$$2\,R\cdot \longrightarrow R-R$$

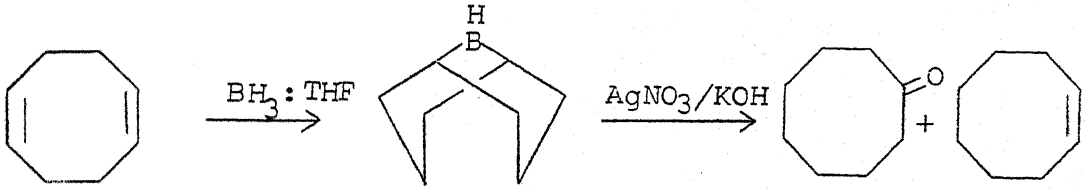
Intramolecular coupling products from cyclic organoboranes have been demonstrated by Murphy and Prager[7,8] (Scheme V.4):

Scheme V.4



However, bicyclic organoboranes from cyclic dienes do not lead to the formation of anticipated bicyclic hydrocarbons.[9] For example, 9-borabicyclo[3.3.1]nonane in tetrahydrofuran on treatment with aqueous silver nitrate (1:1 molar ratio) and potassium hydroxide at 10° gave a mixture of cyclooctanone (85%) and (Z)-cyclooctene (15%) as shown in Scheme V.5. Dihydroboration of internal acetylenes such as 5-decyne, 2-nonyne, diphenylacetylene and cyclotridecyne followed by excess of silver nitrate treatment proceeds to give the corresponding olefins in good yields.[10]

Scheme V.5

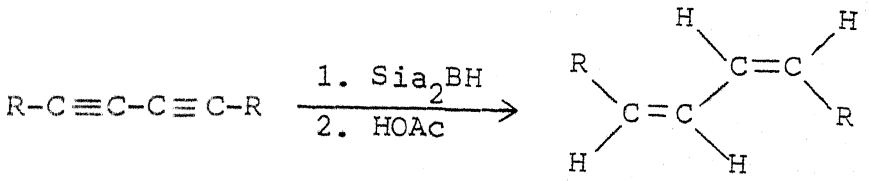


Silver oxide and auric oxide[11] have also been found to be good reagents for coupling of organoboranes. Coupling with reagents such as lithium dimethyl cuprate, cupric chloride, cuprous chloride[12] and platinic oxide[11] was unsuccessful.

Conjugated 1,3-dienes are valuable intermediates in organic syntheses, most notably in Diels-Alder reaction.[13] Of late, considerable attention has been focussed on the synthesis of these compounds and a number of interesting methods employing vinylmetallic reagents have been reported in recent years.[12,14-40]

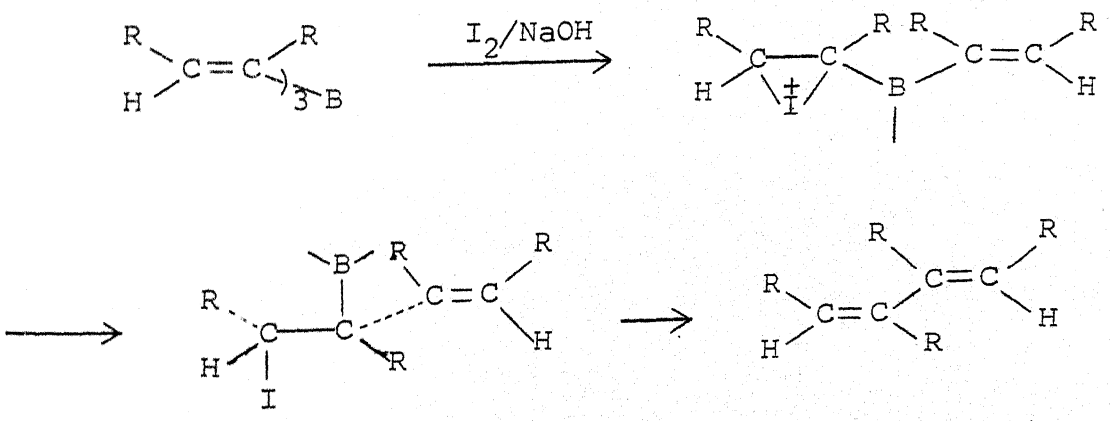
(Z,Z)-Dienes are readily synthesized from diacetylenes *via* hydroboration protonolysis reaction[16] (Scheme V.6):

Scheme V.6



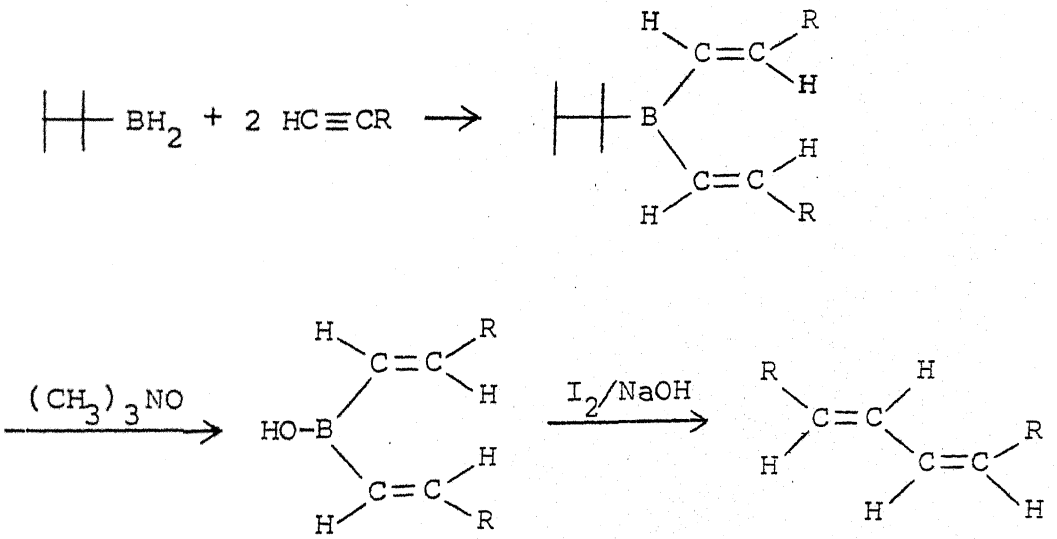
The hydroboration of disubstituted alkynes with borane in a 3:1 ratio in tetrahydrofuran solvent gives the corresponding trivinylboranes.[41,42] Addition of iodine and sodium hydroxide to the tetrahydrofuran solution of the trivinylborane gives (Z,E)-dienes.[14] The formation of the (Z,E)-diene may be rationalized in terms of an initial addition of iodine to the double bond, followed by subsequent migration of a vinyl group from boron to the adjacent carbon atom to give the β-iodoorganoboranes (Scheme V.7):

Scheme V.7



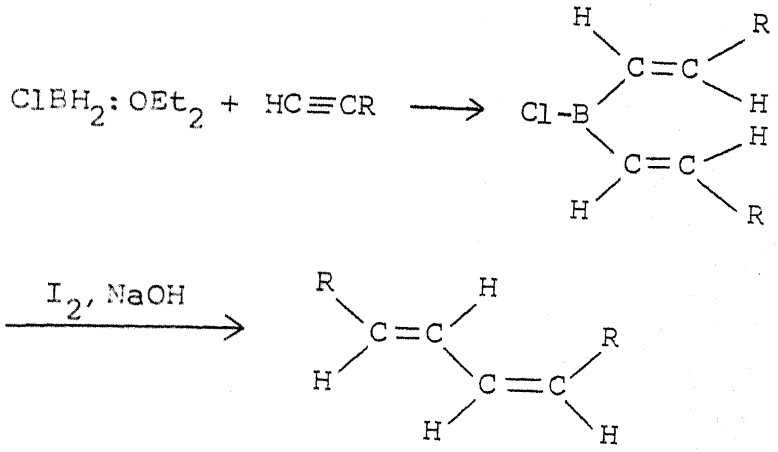
It has been suggested that the migration of an alkyl group, which results from the iodination of a dialkylvinylborane, proceeds with inversion at the migration terminus, and that deboronoiodination occurs in a trans manner. The hydroboration of terminal alkynes results predominantly in the formation of 1,1-diboroalkanes.[41] However, thexylborane reacts with terminal alkynes to give divinylthexylboranes.[43] But addition of iodine, and sodium hydroxide results in migration of both the vinyl and thexyl moieties. This problem has been alleviated by using trimethylamine oxide (Scheme V.8). This procedure has been

Scheme V.8



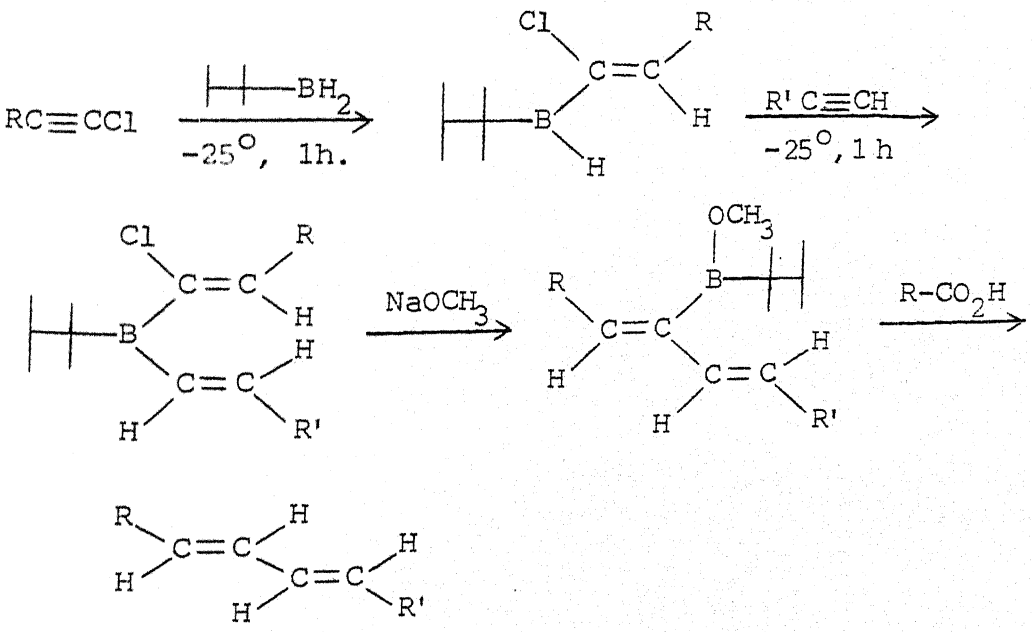
shortend considerably by utilizing chloroborane etherate for the hydroboration[18] (Scheme V.9):

Scheme V.9



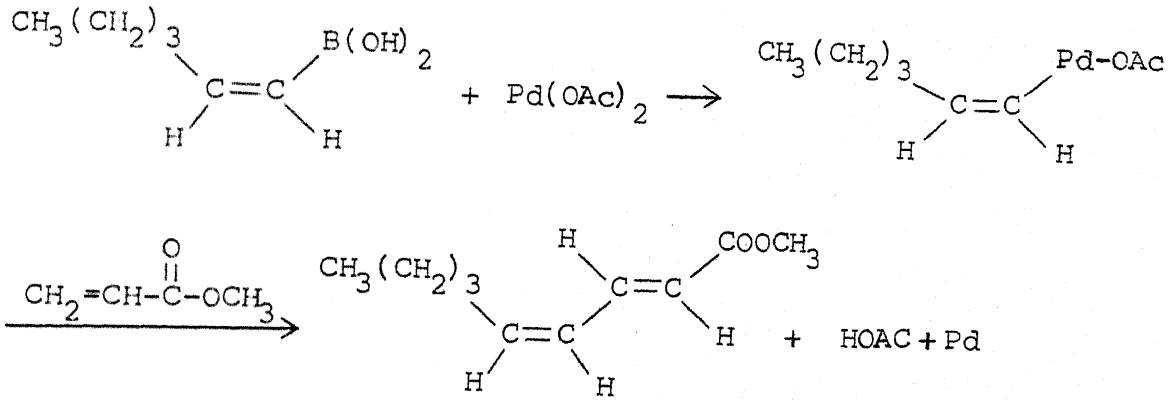
1-Chloroalk-1-ynes react with thexylborane at -25° to produce 1-chloroalk-1-enyl(1,1,2-trimethylpropyl)boranes which can hydroborate terminal alkynes to give mixed organoborane. Treatment of the mixed organoborane with sodium methoxide followed by protonolysis, provides the corresponding (E,E)-dienes[17] (Scheme V.10):

Scheme V.10



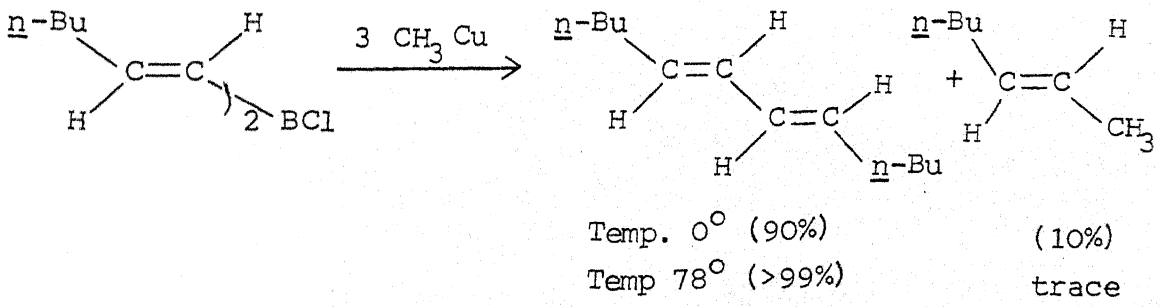
The reactions of (Z)- and (E)-1-hexenylboronicacids with stoichiometric amounts of palladium acetate in presence of methyl acrylate at 0° provided methyl (E,Z)-2,4-nonadienoate and methyl (E,E)-2,4-nonadienoate in 70 and 82% yield respectively[29] (Scheme V.11):

Scheme V.11



Dialkenylchloroboranes react with three molar equivalents of methyl copper to produce symmetrical (E,E)-1,3-dienes in high yield[12,33] (Scheme V.12):

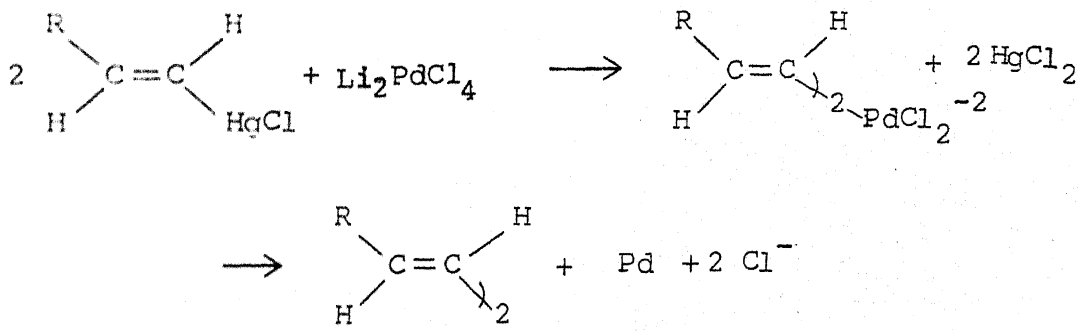
Scheme V.12



The similar reaction with alkenyldisiamylboranes or alkenyldicyclohexylboranes produces (E,E)-1,3-dienes in moderate yields along with a considerable amount of by products.[12] In these reactions, it is essential to utilize three molar equivalents of methylcopper in order to achieve the effective conversion of the boranes to dienes.

Symmetrical dimerization of vinylmercuric chlorides using stoichiometric amounts of palladium chloride and lithium chloride provided 1,3-dienes in excellent yield[31] (Scheme V.13):

Scheme V.13



It has been suggested that these coupling reactions proceed through initial exchange to form a dichlorodivinylpalladium dianion which then reductively eliminates the diene, chloride anion and palladium metal. The reaction was carried out at $0^{\circ}C$ in HMPA. This procedure suffered a few disadvantages viz., (i) it required stoichiometric amounts of expensive palladium chloride, (ii) to achieve high stereospecificity the reaction had to be carried out at temperatures close to that at which HMPA begins

to solidify, (iii) the solvent of choice, HMPA, has since been found to be carcinogenic.[31] Vedejs and Weeks reported a similar reaction employing cis and trans-dipropenylmercury and catalytic amounts of tetrakis(triphenylphosphine)palladium(0),[30] (Scheme V.14). Unfortunately divinylmercurials are generally

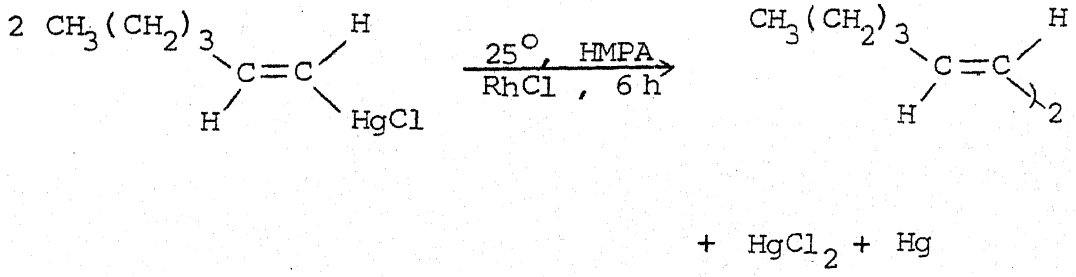
Scheme V.14

$$(CH_3CH=CH)_2Hg \xrightarrow{\text{cat. } Pd(PPh_3)_4} (CH_3CH=CH)_2 + Hg$$

liquids and thus more difficult to handle and puify than the corresponding vinylmercuric chlorides. Furthermore, owing to their greater volatility, they are presumably much more toxic. This catalytic procedure also proceeds with 4-8% loss of stereospecificity.

Both rhodium(I) and (III) complexes very effectively catalyze the dimerization of vinylmercuric chlorides, to provide excellent yields of isomerically pure 1,3-dienes[32] (Scheme V.15):

Scheme V.15



$$+ HgCl_2 + Hg$$

It is believed that the Vinylmercury dimerization reactions involve, a transfer of the organic moiety from mercury to

rhodium producing mercuric chloride and an organorhodium(I) species, an oxidative addition across the carbon-mercury bond of a second equivalent of organomercurial to produce rhodium(III) species and a reductive elimination of the organic dimer which regenerates the rhodium(I) catalyst and metallic mercury (Scheme V.16):

Scheme V.16

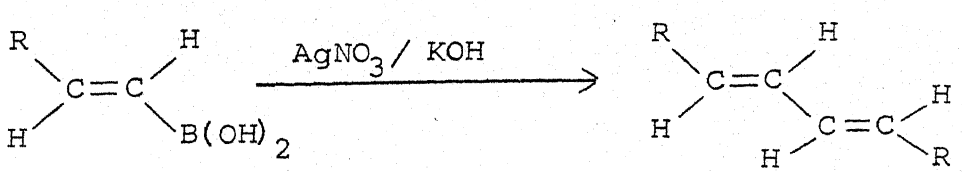
$$R\text{-}HgCl + RhCl \longrightarrow Rh\text{-}R + HgCl_2$$

$$Rh\text{-}R + R\text{-}HgCl \longrightarrow R_2Rh\text{—}HgCl$$

$$R_2Rh\text{-}HgCl \longrightarrow R\text{-}R + RhCl + Hg$$

Alkenyl halides were often employed as starting materials in these reactions. However, the synthesis of the requisite stereodefined alkenyl halide is sometimes cumbersome. To overcome this difficulty the direct use of alkenylboronicacids stereoselectively obtainable *via* hydroboration of acetylenes appeared to be more promising. As organoboranes are known to couple with silver nitrate[3-8] we directed our attempts towards the syntheses of (*E*,*E*)-1,3-dienes from the corresponding vinylboronicacids (Scheme V.17):

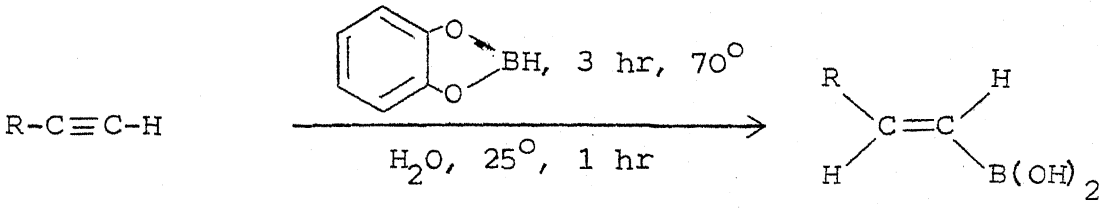
Scheme V.17



V.3 RESULTS AND DISCUSSION

The vinylboronicacids used in the present investigation were prepared by hydroboration with catecholborane followed by hydrolysis with water of the corresponding acetylenes[44] like 1-nonyne, phenylacetylene, p-methylphenylacetylene and p-methoxyphenylacetylene (Scheme V.18). However, our attempts to prepare

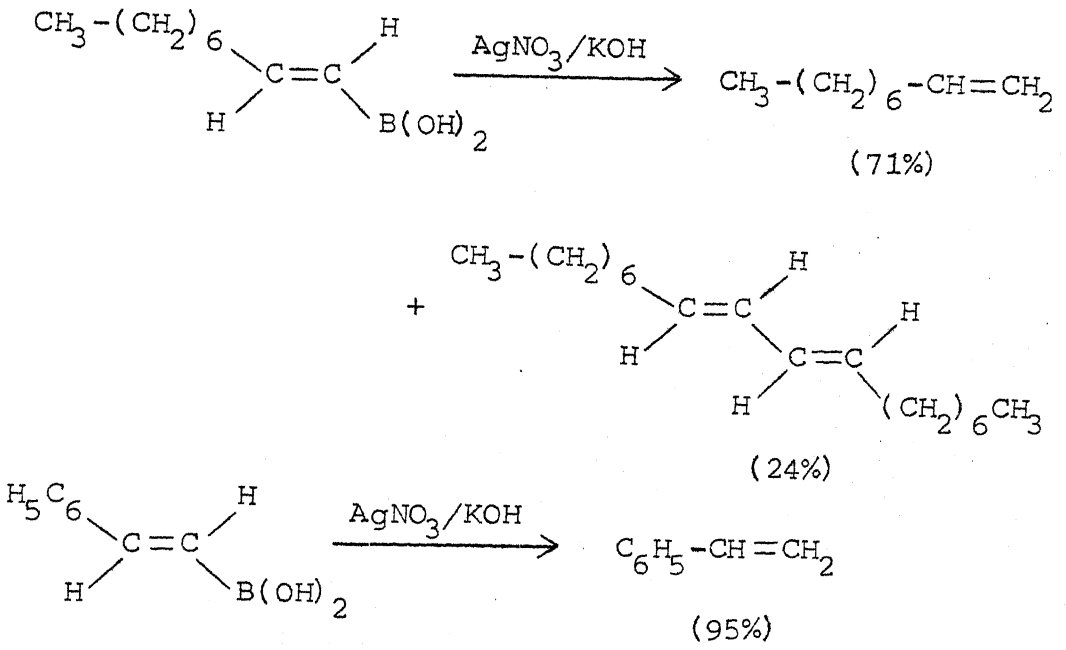
Scheme V.18



the vinylboronicacids from 5-decyne, diphenylacetylene and 1-phenylpropyne have met with failure. The boronicacids thus obtained were readily characterized by their IR spectra, which showed a broad absorption near 3200 cm^{-1} (ν O-H), 1620 cm^{-1} (ν $\backslash C{=}C{-}H$ / H) and 1000 cm^{-1} (δ H$\backslash C{=}C{-}H$ /). NMR spectra display an olefinic proton as a doublet ($J = 18$ Hz) between δ5.5-6.0. All boronicacids gave satisfactory elemental analyses.

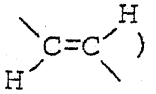
The reaction of trans-β-n-heptylethynylboronicacid with aqueous silver nitrate and methanolic potassium hydroxide gave 1-nonene in 71% yield (GLC analysis), and (E,E)-8,10-octadecadiene in 24% yield (Scheme V.19). 1-Nonene was identified by GLC retention times and IR spectrum with that of an authentic sample. The IR spectrum of (E,E)-8,10-octadecadiene showed absorptions at 3020 cm^{-1} (ν =C-H) and 980 cm^{-1} (δ H$\backslash C{=}C{-}H$ /).

Scheme V.19

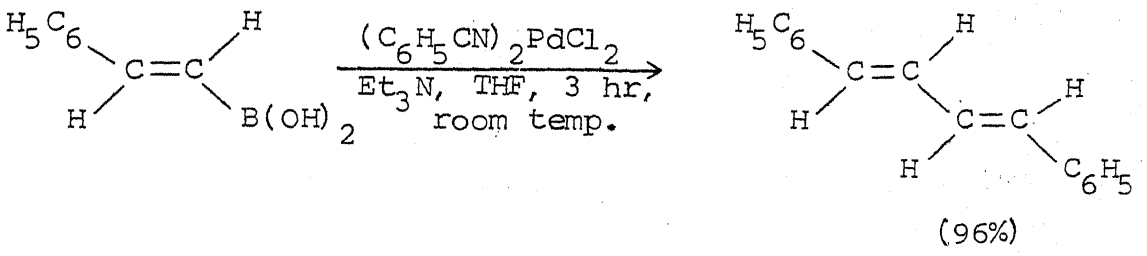


Its NMR displayed a multiplet of four protons at δ5.17-6.33. Its UV showed an absorption at 232 nm (log ε = 4.56). It gave satisfactory elemental analysis and a ^{13}C NMR spectrum. trans-β-Phenylethenylboronicacid under similar conditions yielded styrene in 95% yield (GLC analysis)(Scheme V.19). This was readily identified by GLC retention times and IR spectrum with that of an authentic sample.

When our work was in progress Larock reported the syntheses of (E,E)-symmetrical dienes from vinylmercurials using palladium[31] and rhodium[32] salts. This prompted us to examine the behaviour of our vinylboronicacids with palladium salt. The reaction of bis(benzonitrile)palladium(II) chloride with trans-β-phenylethenylboronicacid gave (E,E)-1,4-diphenyl-1,3-butadiene

in quantitative yield (Scheme V.20). This was readily identified by its IR which showed an absorption at 990 cm^{-1} (δ ) and NMR displayed four protons at δ6.4-7.05 as a multiplet.

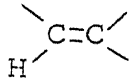
Scheme V.20



(96%)

The high stereospecificity and quantitative yeilds of this interesting reaction prompted us to optimise the conditions by varying the ratio of reactants. Eventually we found that, in the presence of excess of lithium chloride, the same conversion can be brought about with only catalytic amounts bis(benzonitrile)palladium(II) chloride and stirring at room temperature for 24 hours in presence of triethylamine.

trans-β-n-Heptylethenylboronicacid on treatment with bis(benzonitrile)palladium(II) chloride (1:0·1 mol, respectively) in presence of excess of lithium chloride and triethylamine, in tetrahydrofuran after stirring for 24 hours, gave 1-nonene in 14% yield, and a mixture of (Z,Z); (Z,E) and (E,E)-8,10-octadecadienes in 76% yield, in the ratio of 3:30:67. The (E,E)- and (Z,E)-8,10-octadecadienes were separated by preparative GLC on a SE-30 column. The (E,E)-8,10-octadecadiene was identical in all respects (IR, NMR, UV and GLC retention times) with that

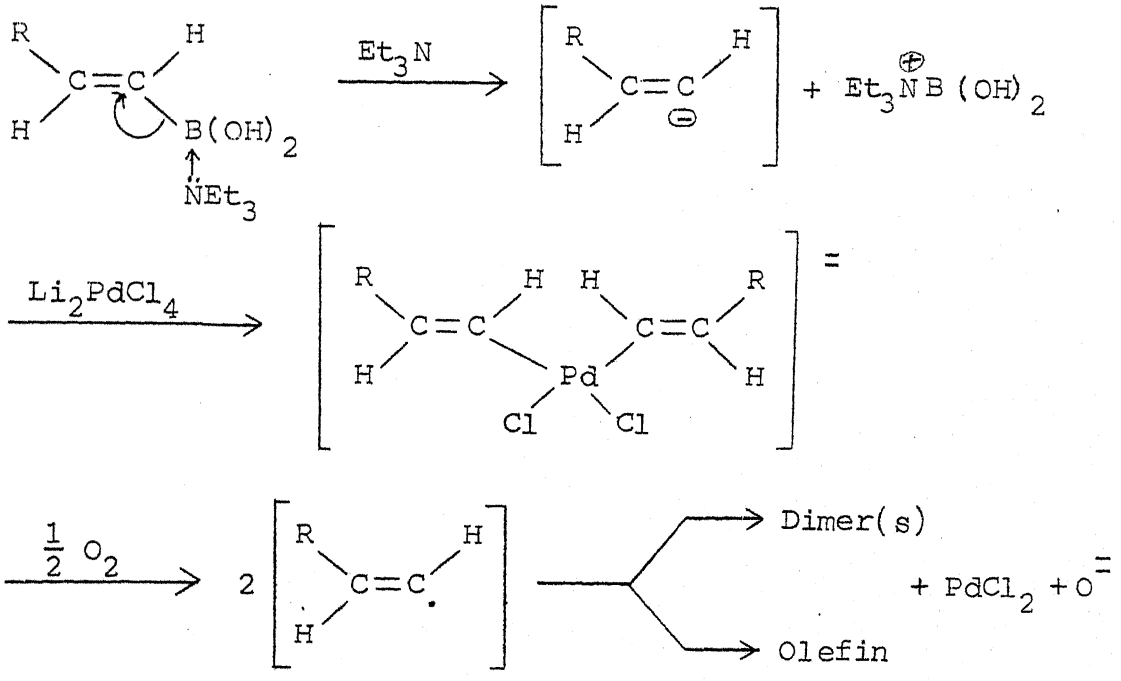
of the sample obtained from silver nitrate reaction. The (Z,E)-8,10-octadecadiene was identified by its IR which showed absorptions at 3020 (ν_{asym} =C-H), 2975 (ν_{sym} =CH), 955 (δ ) and 710 cm^{-1} (δ ). Its NMR spectrum displayed a multiplet for four protons at δ 4.66-6.66. Its UV spectrum shows an absorption maximum at 233 nm (log ε = 4.54). In general the retention times on SE-30 decreased along the series (Z,Z) < (Z,E) < (E,E).[12] So by analogy we expected that the peak with less retention time to be (Z,Z)-8,10-octadecadiene. During the course of our work we used palladium chloride instead of bis(benzonitrile)palladium chloride and obtained almost identical results.

This interesting stereospecific reaction prompted us to examine its generality for the syntheses of (E,E)-1,4-diaryl-1,3-butadienes. Accordingly when we treated trans-β-p-methylphenylethenylboronicacid and trans-β-p-methoxyphenylethenylboronicacid with palladium chloride (1:0·1 mol) in presence of excess of lithium chloride and triethylamine, interestingly enough we obtained (E,E)-1,4-bis(p-methylphenyl)-1,3-butadiene and (E,E)-1,4-bis(p-methoxyphenyl)-1,3-butadiene respectively in excellent yield. These were readily identified by their m.p.'s with reported values.[45,46] They gave satisfactory IR and NMR.

A plausible mechanism to account for the products formed may be schematically represented as follows (Scheme V.21). The first step is probably the coordination of base to boron to facilitate, the trans-metallation in the second step to give

divinylpalladium chloride dianion. This intermediate can undergo homolysis to give two vinyl radicals.

Scheme V.21



Detailed analysis of the ESR spectra of vinyl radicals is consistent with a bent formulation with rapid inversion of its configuration even at -180°.[47] It was also shown that vinyl radicals undergo inversion faster than hydrogen abstraction in some examples, giving rise to cis and trans olefins.[48] It was demonstrated that, when two radicals are generated in the same solvent cage, simultaneously, they predominantly couple.[49,50] Kochi has demonstrated that the radical couplings are sensitive to the viscosity of the solvent using diacylperoxides. Larger the viscosity,[51] more symmetrical dimer was formed. Radicals can rotate many times within the solvent cage prior to combination.[52,53]

In the proposed mechanism both radicals are generated in the same solvent cage,[49,50] there is a high probability for coupling to occur to give the dienes. This was infact observed. Since vinyl radicals were known to undergo inversion[47,52,53] even at low temperatures one would expect a mixture of (E,E); (Z,E) and (Z,Z) dienes in decreasing yields. This was found to be true in the case of trans-β-n-heptylethenylboronicacid which gave a mixture of (E,E), (Z,E) and (Z,Z)-8,10-octadecadienes in the ratio 67:30:3 respectively. The vinyl radical may also abstract a hydrogen atom from the solvent[48] to give an olefin. Thus 1-nonene was obtained in 14% yield. Hydrogen abstraction by radicals is more facile in alcoholic solvents than in ether solvents.[51] When the reaction was carried out in iso-propanol the yield of 1-nonene has increased to 35%. In the case of phenylethenylboronicacid, the coupling seems to be very fast so that one cannot observe hydrogen abstraction or inversion. The inversion energy for this radical being high,[54] exclusive formation of (E,E)-1,4-diphenyl-1,3-butadiene was observed. When the reaction was carried out in presence of styrene and 2-cyclohexen-1-one, there was no change in the product composition. Styrene and 2-cyclohexen-1-one were found unreacted after the reaction. This rules out the possibility of π-allylpalladium intermediates in the reaction.[36] In the last step of the proposed mechanism we explained the recycling of palladium chloride by taking into consideration atmospheric oxygen.

In fact, when the reaction was carried out in nitrogen atmosphere there was a marked decrease in the yield of the product. Similar was the result when lithium chloride was absent. This is understandable as Li_2PdCl_4 is known to be more reactive than palladium chloride itself.

Thus, the present investigation clearly demonstrates the high stereospecificity of the palladium chloride coupling reactions, with particular reference to arylethenylboronicacids. The obvious advantages of this procedure are: (i) the vinylboronicacids can be prepared conveniently and stereospecifically from the corresponding acetylenes by hydroboration procedure.[44] (ii) A common solvent like tetrahydrofuran can be used successfully without recourse to HMPA. (iii) The reaction goes to completion with catalytic amounts of palladium salt at room temperature and in free atmosphere. Hence the present procedure is extremely useful and convenient for the syntheses of (E,E)-1,4-diaryl-1,3-butadienes. The reaction of trans-β-n-heptylethenylboronicacid gives important clues to the reaction pathway although synthetically not very useful. Further, trans-β-p-methylphenylethenylboronicacid and trans-β-p-methoxyphenylethenylboronicacid and (E,E)-8,10-octadecadiene are reported for the first time in literature.

V.4 EXPERIMENTAL

Boiling points are uncorrected. Melting points were taken on a Fischer-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on Beckman IR-8 Spectrometer

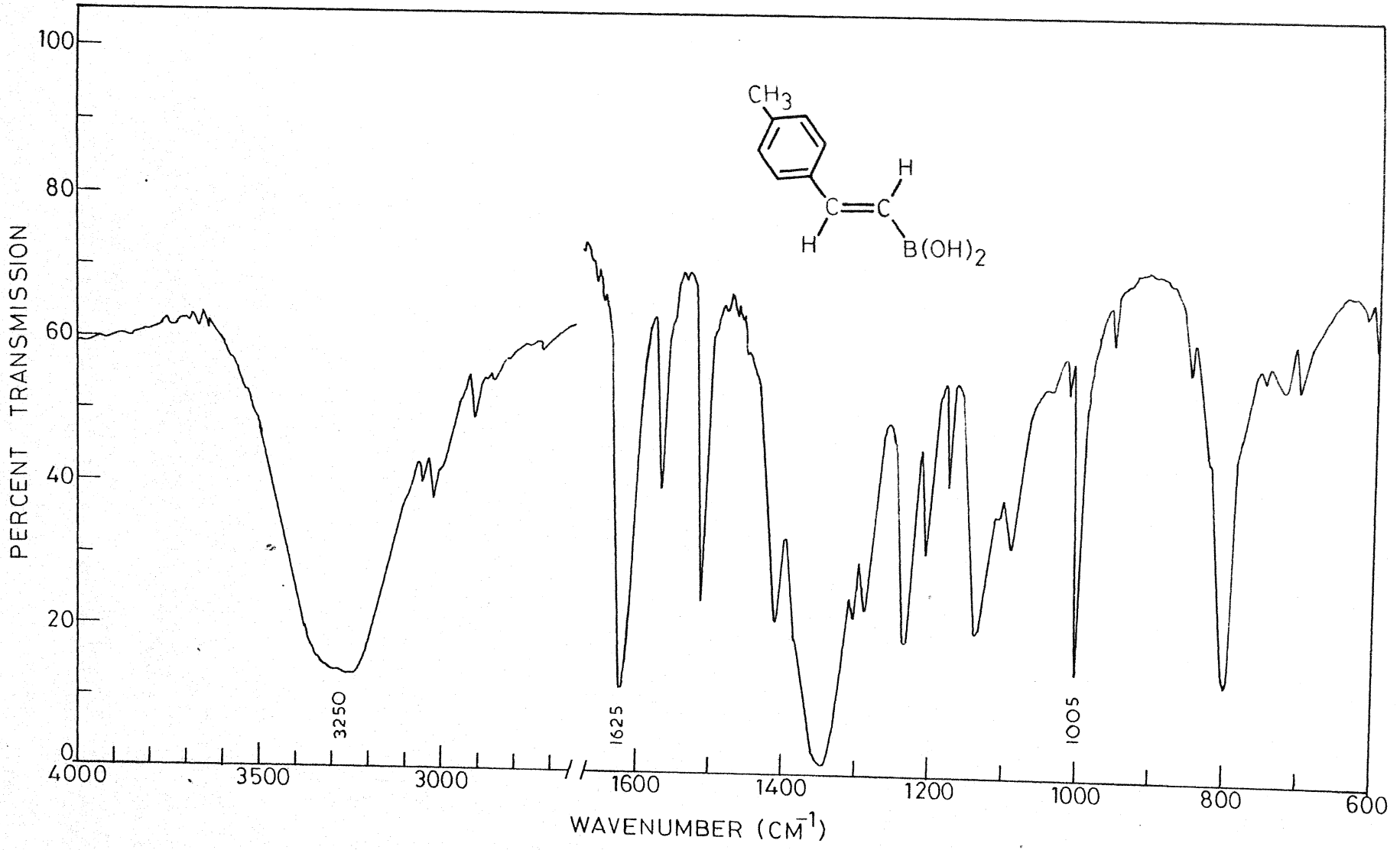


Fig. V.1 , IR spectrum of trans-β-p-methylphenylethenylboronicacid .

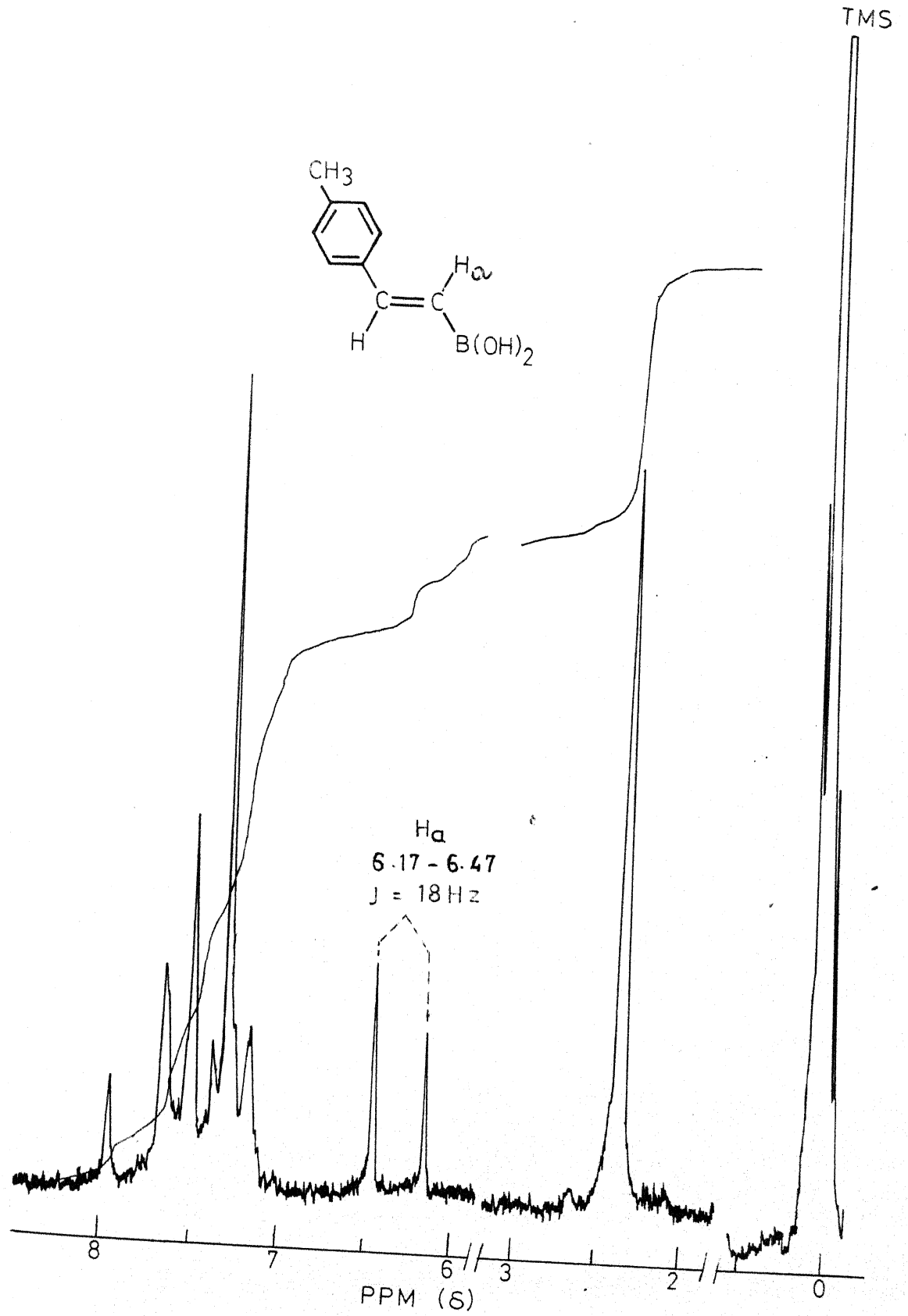


Fig.V.2 NMR spectrum of trans-β-p-methylphenylethenylboronicacid.

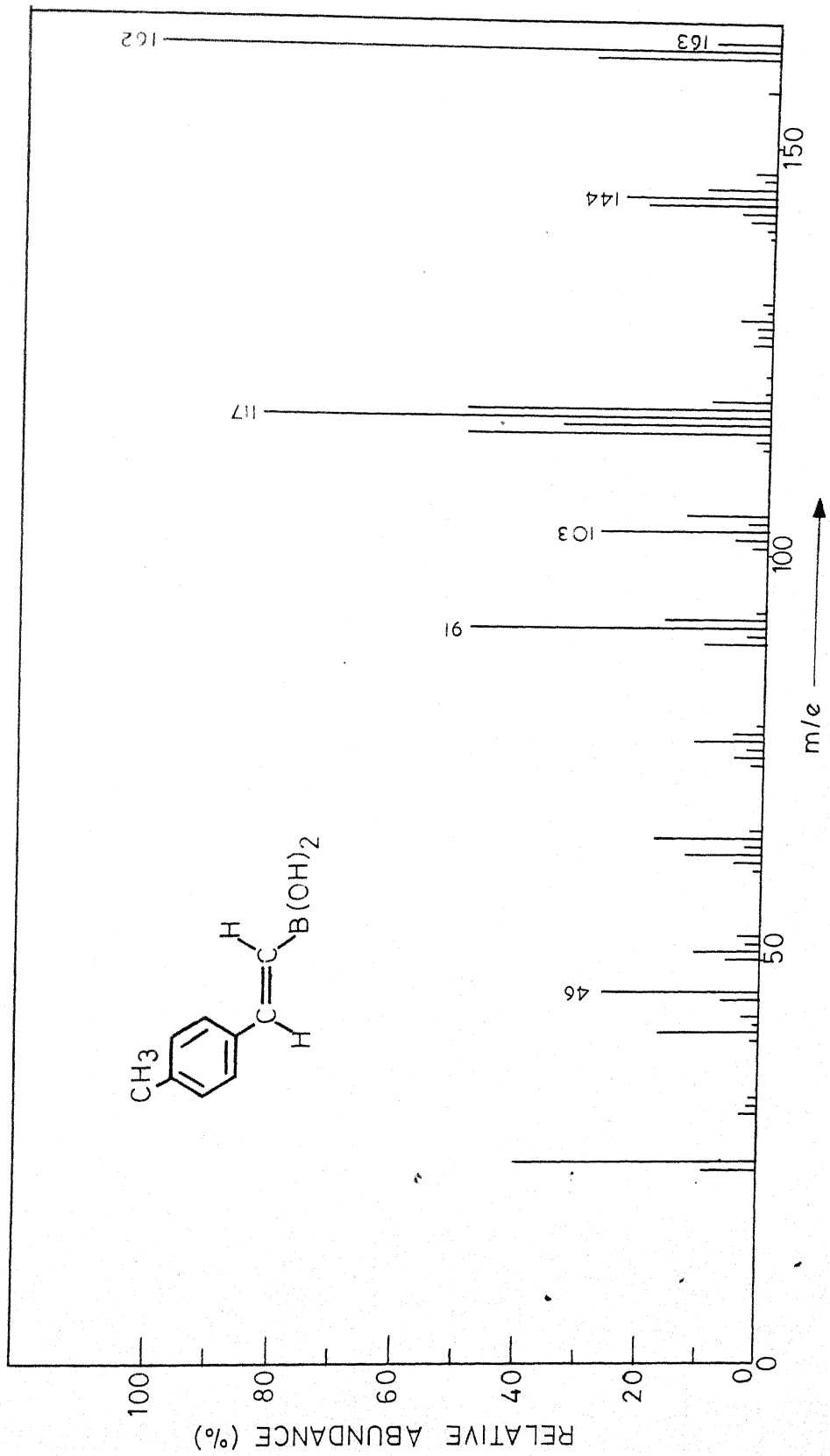


Fig. V.3 Mass spectrum of trans-β-p-methylphenylethenylboronicacid.

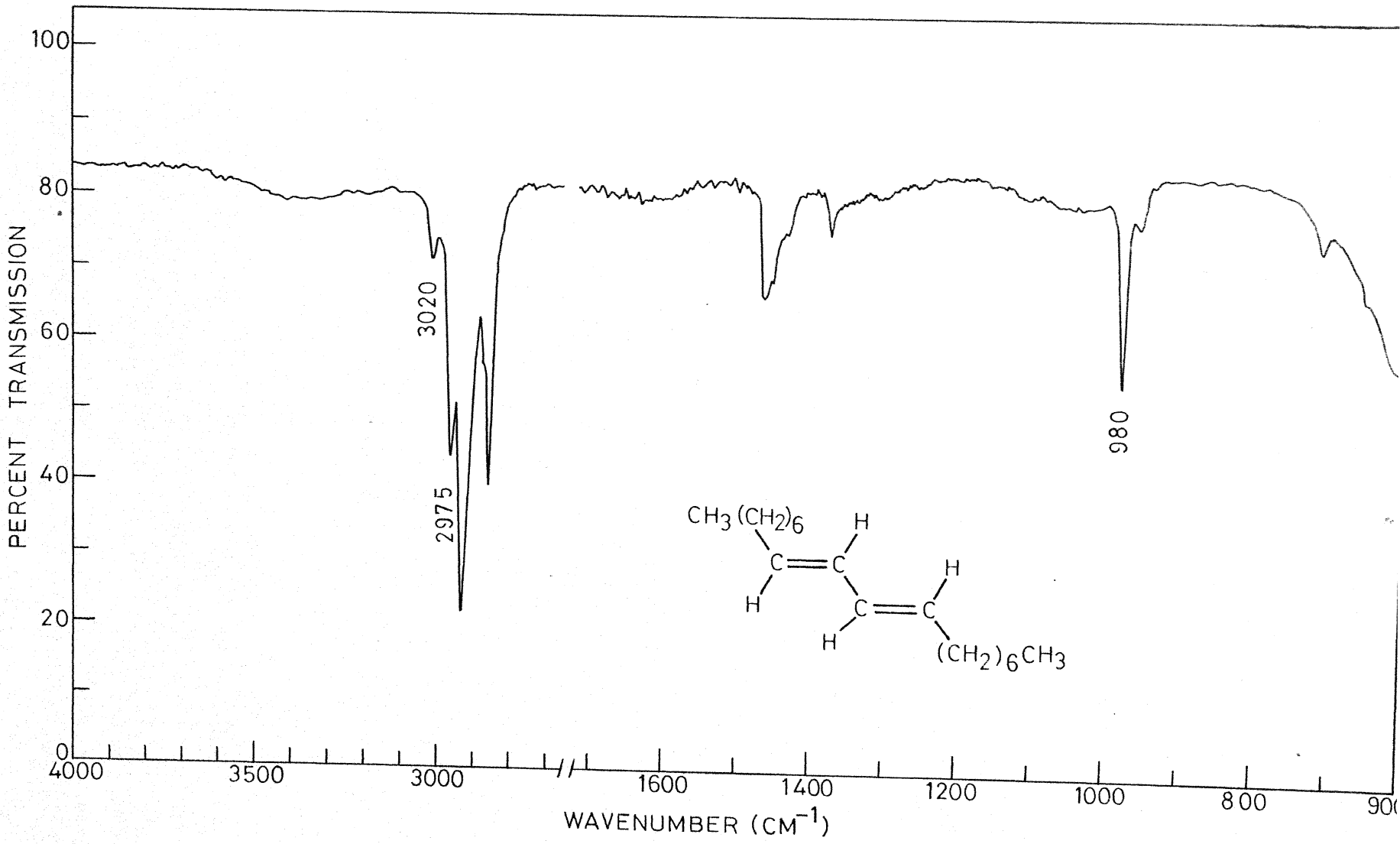


Fig.V.4 IR spectrum of (E,E)-8,10-octadecadiene.


CH3 (CH2)6
Ha
Ha
Ha
Ha
(CH2)6 CH3
TMS
Ha
5.17–6.33
7
6
5
2
1
0
PPM (δ)

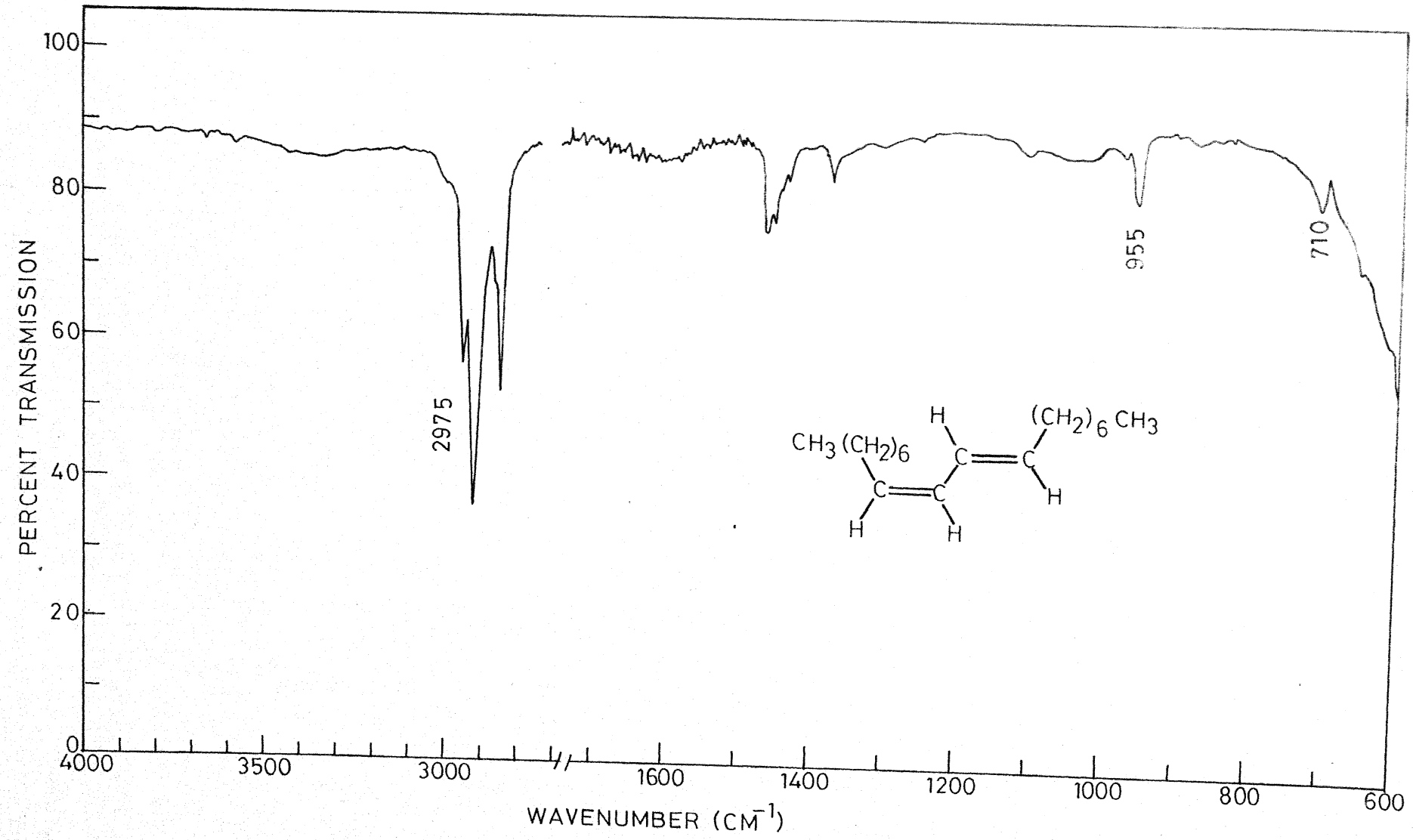
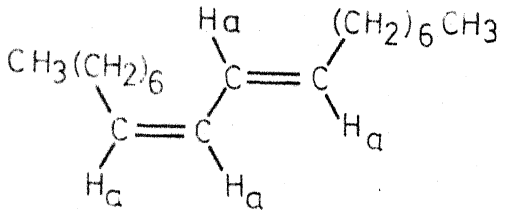


Fig. V.6 IR spectrum of (Z,E)-8,10-octadecadiene.



Ha
4·66–6·66

7 6 5 2 1 0

PPM (δ)

using potassium bromide discs or as liquid between sodium chloride plates or in carbon tetrachloride solvent. Nuclear magnetic resonance spectra were recorded on a Bruker WH-90 Spectrometer employing deuterated chloroform as solvent and tetramethylsilane as an internal standard. Gas Liquid Chromatographic analyses were done with Aerograph Model Varian 90-P Instrument. ^{13}C NMR was recorded on Varian XL-100 Instrument. UV Spectra were recorded on Toshniwal mannual UV spectrophotometer or on Varian Super Scan-3 spectrometer. The mass spectra were recorded on EKB 9000. Microanalyses were carried out by Mr. A.H. Siddiqui of the Department of Chemistry, Indian Institute of Technology, Kanpur. India.

Materials

Catechol (E. Merck) was recrystallised twice from toluene and dried before use. Tetrahydrofuran (BDH), p-methylacetophenone (Aldrich) styrene (BDH), p-methoxystyrene (K & K), n-heptylbromide (Fluka), were used after purification by distillation. Boron trifluoride etherate (Aldrich) and diglyme (Ansul Co.) were dried and distilled before use. Acetylene (IOL) was purified by passing through two traps of concentrated sulphuric acid. Sodium (Pfizer), phosphorous pentachloride (Pfizer), potassium hydroxide (Sarabhai), palladium chloride (SISCO), lithium chloride (Austranal), sodium borohydride (BDH) and other substances were used without further purification.

Preparation of 1-Nonyne[55]

Sodium (8.8 g, 0.38 g.atom) was converted to sodium acetylide in a 1 l.. three necked flask by adding sodium in small pieces to liquid ammonia (500 ml) while bubbling acetylene through ammonia during 30 minutes. The mixture was stirred for additional 15 minutes. The gas inlet tube was then replaced by a dropping funnel. n-Heptylbromide (68 g , 0.38 mol) was slowly added through the dropping funnel during a period of 2 hours. The reaction mixture was hydrolysed by dropwise addition of water (750 ml) in 90 minutes. The reaction mixture was separated into two layers, the upper layer of which was removed, washed with hydrochloric acid (10%) and then with sodium carbonate (20%) and finally twice with water. The product was dried over calcium chloride and carefully fractionated through an efficient condenser packed with glass spirals to give 1-nonyne (31 g, 0.25 mol) in 67% yield, b.p. 98.5°/15 mm (lit.[56] 51°/8 mm). GLC analysis indicated it to be 99% pure.

IR (neat): 3300 ($\nu \equiv CH$), 2100 cm^{-1} (ν C$\equiv$CH).

NMR ($CDCl_3$), δ ppm: 2-2.35 (2H, m), 1.9 (1H, t, J = 2.2 Hz), 1.1-1.6 (10 H, s), 0.9 (3H, t, J = 5 Hz).

Preparation of Styrene Dibromide[57]

A solution of freshly distilled styrene (206 g, 2 mmol) in dry chloroform (200 ml) is taken in a litre beaker, cooled in an ice bath, and provided with a mechanical stirrer.

A solution of bromine (340 g, 2.15 mol) in chloroform (200 ml) was added slowly through the dropping funnel while stirring at a rate to confirm with discharge of colour from red to pale yellow. After the addition of bromine was over, the stirring was allowed to continue till the reaction was complete. Chloroform was evaporated under vacuum to give styrenedibromide (510 g, 1.94 mol) in 97% yield, m.p. 71-72° (lit.[57] m.p. 73-74°).

Preparation of Phenylacetylene[58]

A 3 l. three-necked flask was equipped with a mechanical stirrer. Liquid ammonia (1000 ml) was condensed in the flask. Ferric nitrate hydrate (1 g) was placed in the flask. Sodium (50 g, 2.18 g.atom) was cut into small pieces and added slowly while stirring in 45 minutes. Aniline (2 g) was added and then finely powdered dry styrenedibromide (264 g, 1 mol) was added gradually with vigorous stirring in 1 hour. Stirring was continued for 2 hours after the addition has been completed, after which concentrated ammonium hydroxide (300 ml) was added, followed by distilled water (500 ml) and the mixture was brought to room temperature. The aqueous solution was then steam-distilled from the same flask till the oil stopped passing over. The phenylacetylene in the distillate was separated and washed several times with distilled water to remove ammonia. The washed material was dried over anhydrous magnesium sulphate and distilled through an efficient column under reduced pressure to give phenylacetylene (50 g, 0.5 mol) in 50% yield,

b.p. 73-74°/80 mm (lit.[59] b.p. 138-140°). GLC analysis indicated it to be 99% pure.

IR (neat): 3300 (ν ≡CH) and 2110 cm^{-1} (ν C≡CH).

NMR ($CDCl_3$), δ ppm: 7-7.5 (5H, m), 2.93 (1H, s).

Preparation of p-Methoxyphenylacetylene

p-Methoxystyrenedibromide (28 g, 0.10 mol) in 95% yield was obtained from p-methoxystyrene (13.4 g, 0.1 mol) and bromir (16 g, 0.1 mol) by following the same procedure for styrene-dibromide preparation, m.p. 72°. From p-methoxystyrenedibromide (28 g, 0.10 mol) and sodamide prepared from sodium (5 g, 0.22g.atom), p-methoxyphenylacetylene (8 g,0.06 mol) was obtained in 62% yield, b.p. 84-86°/27 mm. GLC analysis indicated it to be 99% pure.

IR (neat): 3300 (ν≡CH) and 2110 cm^{-1} (ν C≡CH).

Preparation of p-Methylphenylacetylene[60]

A mixture of phosphorous pentachloride (5 g, 24 mmol) an p-methylacetophenone (5.5 g, 41 mmol) was maintained at 70-80° for 30 minutes. The resulting dark orange solution was distilled and the fraction (4.4 g) boiling between 80-95°/15 mm was collected. This fraction was refluxed overnight with potassiu hydroxide (5 g) in absolute ethanol (5 ml). After adding ice-cold water (150 ml) the solution was extracted with solvent ether, washed with ice cold water and dried over sodium sulpha

Distillation gave p-methylphenylacetylene (2.1 g, 16 mmol) in 38% yield, b.p. 59-60°/16 mm (lit.[61] b.p. 65-67°/18 mm). GLC analysis indicated it to be >98% pure.

IR: 3300 (ν $\equiv$CH) and 2100 cm^{-1} (ν C$\equiv$CH).

NMR ($CDCl_3$), δ ppm: 2.33 (3H, s), 3.03 (1H, s), 7-7.66 (4H, m).

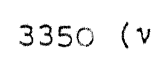
Preparation of Catecholborane[62] (1,3,2-Benzodioxaborole)

A solution of borane in tetrahydrofuran (2 M, 100 ml, 0.2 mol), maintained under nitrogen was placed in a dry 500 ml flask which was connected to a hood vent through a mercury bubbler. The flask was immersed in an ice bath, and a solution of o-dihydroxybenzene (catechol) (22 g, 0.2 mol) in tetrahydrofuran (50 ml) was added over a period of 30 minutes to the borane solution with efficient stirring at 0°. After the completion of the addition, the reaction mixture was stirred at 25° for an additional 30 minutes. Distillation under nitrogen provided catecholborane (17 g, 0.14 mol) in 71% yield, b.p. 76-77° 100 mm (lit.[63] b.p. 88°/156 mm).

Preparation of trans-β-Phenylethylboronicacid[44]

A mixture of phenylethyne (3 g, 29 mmol) and catecholborane (4 g, 33 mmol) was stirred under nitrogen atmosphere at 75° for 2 hours. The flask and the contents were cooled to room temperature under nitrogen and stirred with water (30 ml) for

1 hour at 80°. Upon cooling a white crystalline compound (4.15 g, 28 mmol) was obtained in 95% yield. The product was recrystallised from water to give pure trans-β-phenylethylboronicacid as cubic crystals, m.p. 163-164° (lit.[44] m.p. 163-164°).

IR: 3350 (νOH), 1620 (ν ), 990 cm^{-1} (δ).

NMR ($CDCl_3$), δ ppm: 7.3-7.8 (8H, m), 6.33 (1H, d, J = 18Hz).

UV , λ_{max} (EtOH): 262 nm (log ε = 4.38).

Anal. for $C_8H_9BO_2$: Calcd C, 64.86; H, 6.08.

Found C, 64.52; H, 5.39%.

Mass Spectrum (70 eV): m/e (rel. abundance), 149 (30), 148 (62), 130 (50), 103 (58), 91 (53), 77 (58), 57 (50), 45 (57), 18 (100).

Preparation of trans-β-n-Heptylethenylboronicacid

By following the procedure described above, from 1-nonyne (2.48 g, 20 mmol) and catecholborane (2.7 g, 22 mmol), trans-β-n-heptylethenylboronicacid (2.1 g, 12.5 mmol) was obtained in 63% yield, m.p. 65-66° (lit.[64] m.p. 67-68°).

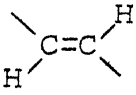
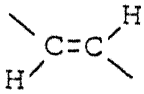
IR (KBr): 3200 (νOH), 1640 (ν) and 1000 cm^{-1} (δ).

NMR ($CDCl_3$), δ ppm: 6.3-7.3 (1H, m), 5.5 (1H, d, J = 18 Hz), 3.73 (1H, s), 2.1 (1H, s), 1.97-2.5 (2H, s), 1.1-1.6 (10H, s), 0.8-1.1 (3H, s).

Anal. for $C_9H_{19}BO_2$: Calcd C, 63.53; H, 11.18.
Found C, 63.12; H, 12.51%.

Preparation of trans-β-p-Methylphenylethenylboronicacid

By following the procedure described for the preparation of trans-β-phenylethenylboronic acid, from p-methylphenylacetylene (0.58 g, 5 mmol) and catecholborane (0.66 g, 5.5 mmol), trans-β-p-methylphenylethenylboronicacid (0.45 g, 2.8 mmol) was obtained in 56% yield, m.p. 126-127°.

IR (KBr): 3250 (ν O-H), 1625 (ν ) and 1005 cm^{-1} (δ ).

NMR ($CDCl_3$), δ ppm: 7.1-7.3 (7H, m), 6.3 (1H, d, J = 18 Hz), 2.37 (3H, s).

UV, λ_{max} (EtOH): 267 nm (log ε = 4).

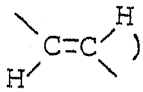
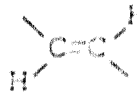
Mass Spectrum (70 eV): m/e (rel. abundance); 163 (10), 162 (100), 144 (24), 117 (83), 103 (27), 91 (49), 46 (26).

Anal. for $C_9H_{11}BO_2$: Calcd C, 66.66; H, 6.79.
Found C, 66.91; H, 6.50%.

Preparation of trans-β-p-Methoxyphenylethynylboronicacid

By following the same procedure described for the preparation of trans-β-phenylethenylboronicacid, from p-methoxyphenylacetylene (1.32 g, 10 mmol) and catecholborane (1.30 g, 11 mmol), trans-β-p-methoxyphenylethenylboronicacid (1.00 g, 0.56 m mol) was

obtained in 56% yield, m.p. 173-174°.

IR (KBr): 3300 (ν O-H), 1620 (ν ) and 1000 cm^{-1} (δ ).

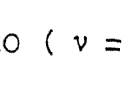
NMR ($CDCl_3$), δ ppm: 7.8 (2H, s), 7-7.6 (5H, m), 6.1 (1H, d, J = 18 Hz), 3.3 (3H, s).

Anal. for $C_9H_8O_3B$: Calcd C, 60.67; H, 6.18.
Found C, 60.53; H, 6.25%.

Silver Nitrate Reaction of trans-β-n-Heptylethenylboronicacid

To trans-β-n-heptylethenylboronicacid (1.7 g, 10 mmol) in tetrahydrofuran, methanolic potassium hydroxide (2 M, 10 ml, 20 mmol) was added drop by drop while stirring the solution vigorously. Aqueous silver nitrate (5 M, 4 ml, 20 mmol) was added quickly at room temperature and allowed to stir for 2 hours. The contents of the flask were centrifuged and the supernatant liquid was extracted with cyclohexane thrice, washed with water till neutral and dried over anhydrous magnesium sulphate. The solvent was removed on a rotatory evaporator. GLC analysis at this stage on a carbowax 10' column revealed the presence of 1-Nonene (900 mg, 7.1 mmol) in 71% yield. 1-Nonene was readily identified by comparing IR spectrum with that of an authentic sample and GLC retention times. The concentrated product mixture at this stage was charged over silica-gel short column and eluted with petroleum ether. The solvent was removed on a rotatory evaporator and the olefin under high vacuum

(0.05 mm) at room temperature. Then the contents were transferred into a molecular distillation flask and distilled to give (E,E)-8,10-octadecadiene (300 mg, 1.2 mmol) in 24% yield, b.p. 110-115°/0.1 mm. GLC analysis on SE-30, 5' column indicated it to be pure.

IR (neat) : 3020 (ν = C-H) and 980 (δ ).

NMR ($CDCl_3$), δ ppm: 5.17-6.33 (4H, m), 1.8-2.3 (4H, s), 1-1.8 (20H, s), 0.83-1 (6H, s).

^{13}C NMR ($CDCl_3$), δ ppm : 134.7 (2C), 133.6 (2C), 35.56 (2C), 34.82 (2C), 32.47 (2C), 32.19 (4C), 25.62 (2C), 16.64 (2C).

UV, λ_{max} (EtOH) : 232 nm ($\log \epsilon = 4.56$).

Anal. for $C_{18}H_{34}$: Calcd C, 86.40; H, 13.60.
Found C, 86.80; H, 13.70%.

Silver Nitrate Reaction of trans-β-Phenylethenylboronicacid

trans-β-Phenylethyenylboronicacid (1.48 g, 10 mmol) was dissolved in tetrahydrofuran (50 ml). Then methanolic potassium hydroxide (2 M, 10 ml, 20 mmol) was added while stirring the solution vigorously. Aqueous silver nitrate (5 M, 4 ml, 20 mmol) was added quickly at room temperature and allowed to stir for 2 hours. The contents of the flask were centrifuged and the supernatant liquid was extracted thrice with cyclohexane, washed with water till neutral and dried over anhydrous magnesium sulphate. The solvent was removed on a rotatory evaporator.

GLC analysis at this stage revealed the presence of styrene (988 mg, 9.5 mmol) in 95% yield. It was readily identified by by comparing with an authentic IR.

Preparation of Bis(benzonitrile)palladium(II) Chloride

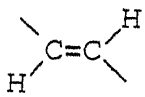
Palladium chloride (2 g, 11 mmol) was dissolved in minimum amount of benzonitrile (approximately 30 ml) at 100°. The solution was filtered while hot and the filtrate on cooling provided the desired product. The heavy precipitate of the complex was filtered and washed with low boiling petroleum ether (40-60°) and dried under vacuum to give bis(benzonitrile)palladium(II) chloride (3.6 g, 9.4 mmol) in 83% yield, m.p. 125-127°.

Anal. for $C_{14}H_{10}N_2PdCl_2$: Calcd C, 43.97; H, 2.67; N, 7.33.
Found C, 44.23; H, 2.74; N, 7.72%

Reaction of Bis(benzonitrile)palladium(II) Chloride with trans-β-Phenylethenylboronicacid

trans-β-Phenylethenylboronicacid (148 mg, 1 mmol), bis-(benzonitrile)palladium(II) chloride (385 mg, 1 mmol) were dissolved in tetrahydrofuran (50 ml) in a 100 ml flask and then triethylamine (5 ml) was added and allowed to stir for 3 hours at room temperature. A black heavy precipitate was separated by centrifuging and the supernatant liquid was washed with water, dilute hydrochloric acid (5%) and dried over anhydrous magnesium sulphate. After concentrating the product it was charged over

a short column of silica-gel and eluted with petroleum ether. The solvent on evaporation gave crystalline (E,E)-1,4-diphenyl-1,3-butadiene (97 mg, 0.47 mmol) in 94% yield, m.p. 152-153° (lit.[45] 154-155°).

IR (KBr): 990 cm^{-1} (δ ).

NMR ($CDCl_3$), δ ppm: 7.15-7.4 (10 H, m), 6.4-7.05 (4H, m).

UV, λ_{max} (EtOH): 347 nm ($\log\varepsilon = 3.87$), 330 nm ($\log\varepsilon = 4.04$), 323 nm ($\log\varepsilon = 4.04$).

Anal. for $C_{16}H_{14}$: Calcd C, 93.19; H, 6.80.
Found C, 93.67; H, 6.72%.

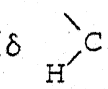
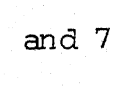
Reaction of Bis(benzonitrile)palladium(II) Chloride with trans-β-Phenylethenylboronicacid in Presence of Lithium Chloride

trans-β-Phenylethenylboronicacid (148 mg, 1 mmol), bis-(benzonitrile)palladium(II) chloride (38 mg, 0.1 mmol), lithium chloride (850 mg, 20 mmol) were dissolved in tetrahydrofuran (50 ml) in a 100 ml round bottom flask. Triethylamine (5 ml) was added and allowed to stir for 24 hours, diluted with petroleum ether and centrifuged. The supernatant liquid was washed with dilute hydrochloric acid (5%), water, and dried over anhydrous magnesium sulphate. Evaporation of the solvent followed by charging the compound over a short column of silica-gel and elusion with petroleum ether gave the crystalline (E,E)-1,4-diphenyl-1,3-butadiene (99 mg, 0.48 mmol) in 96% yield, m.p. 152-153° (lit.[45] m.p. 154-155°).

Reaction of trans-β-n-Heptylethenylboronicacid with Bis(benzonitrile)palladium(II) Chloride in Presence of Lithium Chloride

trans-β-n-Heptylethenylboronicacid (170 mg, 1 mmol), bis-(benzonitrile)palladium(II) chloride (38 mg, 0.1 mmol), lithium chloride (850 mg, 20 mmol) were dissolved in tetrahydrofuran (50 ml) in a 100 ml round bottom flask. Triethylamine (5 ml) was added and allowed to stir for 24 hours, diluted with petroleum ether and centrifuged. The supernatant liquid was washed with dilute hydrochloric acid (5%), water and dried over anhydrous magnesium sulphate. The solvent was evaporated. GLC analysis at this stage on carbowax 10' column showed the presence of 1-nonene (17 mg, 0.14 mmol) in 14% yield. The product mixture was then charged over a short column of silica-gel and eluted with petroleum ether. Evaporation of the solvent and 1-nonene at room temperature under high vacuum (0.05 mm) gave a mixture of (Z,Z), (Z,E), (E,E)-8,10-octadecadienes (95 mg, 0.38 mmol) in 76% yield in the ratio 3:30:67. (E,E)-8,10-Octadecadiene was identical in all respects (IR, NMR, UV & GLC retention times) with the sample obtained earlier in the silver nitrate reaction. (Z,E)-8,10-Octadecadiene was separated by preparative GLC on SE-30 column and identified by its IR, NMR and UV. By analogy with literature[12] the component with less retention time was predicted to be (Z,Z)-8.10-octadecadiene.

(Z,E)-8,10-Octadecadiene

IR (neat): 3020 cm^{-1} (ν_{asym} = C-H), 2975 cm^{-1} (ν_{sym} = C-H), 955 cm^{-1} (δ ) and 710 cm^{-1} (δ ).

NMR ($CDCl_3$), δ ppm: 4.66-6.66 (4H, m), 1.8-2.3 (4H, s), 1.06-1.66 (20H, m), 0.8-1.06 (4H, s).

UV, λ_{max} (EtOH): 233 nm ($\log \varepsilon = 4.54$).

Reaction of Palladium Chloride with trans-β-Phenylethenylboronic-acid in Presence of Lithium Chloride

trans-β-Phenylethenylboronicacid (148 mg, 1 mmol), palladium chloride (18 mg, 0.1 mmol), lithium chloride (850 mg, 20 mmol) were dissolved in tetrahydrofuran (50 ml) in a 100 ml flask and then triethylamine (5 ml) was added and allowed to stir for 24 hours at room temperature. The solution was diluted with petroleum ether, centrifuged and the supernatant liquid was washed with water, dilute hydrochloric acid (5%) and dried over anhydrous magnesium sulphate. After concentrating the product it was charged over a short column of silica-gel and eluted with petroleum ether. The solvent on evaporation gave crystalline (E,E)-1,4-diphenyl-1,3-butadiene (97 mg, 0.47 mmol) in 94% yield, m.p. 152-153° (lit.[45] m.p. 154-155°).

IR, NMR, UV were identical as reported earlier.

Reaction of Palladium Chloride with trans-β-n-Heptylethenyl-boronicacid in Presence of Lithium Chloride

trans-β-n-Heptylethenylboronicacid (170 mg, 1 mmol), palladium chloride (18 mg, 0.1 mmol) and lithium chloride (850 mg, 20 mmol) were dissolved in tetrahydrofuran (50 ml)

in a 100 ml round bottom flask. The reaction was worked up as described above to show 1-nonene (7.5 mg, 0.06 mol) in 6% yield. and a mixture of (Z,Z), (Z, E) and (E,E)-8,10-octadecadienes (90 mg, 0.36 mmol) in 72% yield in the ratio of 3:30:67 respectively.

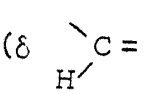
Reaction of Palladium Chloride with trans-β-n-Heptylethenylboronicacid in Presence of Lithium Chloride in Isopropanol

trans-β-n-Heptylethenylboronic acid (170 mg, 1 mmol), palladium chloride (18 mg, 0.1 mmol) and lithium chloride (850 mg, 20 mmol) were dissolved in isopropanol (50 ml) in a 100 ml round bottom flask. The reaction was worked up as described earlier to show 1-nonene (44 mg, 0.35 mmol) in 35% yield.

Reaction of Palladium Chloride with trans-β-p-Methylphenylethenylboronicacid in Presence of Lithium Chloride

trans-β-p-Methylphenylethenylboronicacid (162 mg, 1 mmol), palladium chloride (18 mg, 0.1 mmol) and Lithium chloride (850 mg, 20 mmol) were dissolved in tetrahydrofuran (50 ml) in a 100 ml round bottom flask. Triethylamine (5 ml) was added and allowed to stir for 24 hours, diluted with petroleum ether and centrifuged. The supernatant liquid was washed with dilute hydrochloric acid (5%), water and dried over anhydrous magnesium sulphate. Evaporation of the solvent followed by charging the compound over a short column of silica-gel and elusion with

petroleum ether gave (E,E)-1,4-bis(p-methylphenyl)-1,3-butadiene (110 mg, 0.47 mmol) in crystalline form in 94% yield, m.p. 198° (lit.[45] m.p. 198°).

IR (KBr): 990 cm^{-1} (δ ).

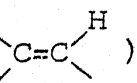
NMR ($CDCl_3$), δ ppm: 7-7.5 (8H, m), 6.66-7 (4H, m), 2.33 (6H, s).

UV, λ_{max} (EtOH): 355 nm ($\log\varepsilon = 4.03$), 337 ($\log\varepsilon = 4.19$), 324 ($\log\varepsilon = 4.10$) and 235 ($\log\varepsilon = 3.58$).

Anal. for $C_{18}H_{18}$: Calcd C, 92.30; H, 7.69.
Found C, 92.29; H, 7.90%.

Reaction of trans-β-p-Methoxyphenylethenylboronicacid with Palladium Chloride in Presence of Lithium Chloride

From trans-β-p-methoxyphenylethenylboronicacid (356 mg, 2 mmol) palladium chloride (40 mg, 0.2 mmol), lithium chloride (1.36 g, 30 mmol), tetrahydrofuran (70 ml) and triethylamine (5 ml), by following the above procedure we obtained (E,E)-1,4-bis(p-methoxyphenyl)-1,3-butadiene (250 mg, 0.94 mmol) in 94% yield, m.p. 222° (lit.[46] m.p. 224-225°).

IR (CCl_4): 1600 (ν ) and 1030 cm^{-1} (δ).

NMR ($CDCl_3$), δ ppm: 6.66-7.3 (12H, m), 3.8 (6H, s).

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